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INVESTIGATIONS ON THE SULPHINIDES.[1]

VII.—ON SOME DERIVATIVES OF BENZOIC SULPHINIDE, AND THE CHANGES CAUSED IN THEIR TASTE BY CHANGES IN COMPOSITION.[2]

BY RUDOLF DE ROODE.

Introduction.

In a paper published in 1887, Remsen and Bayley[3] describe a method for the preparation of para-brom-sulphinide. Among its properties, the most characteristic is that it possesses two separate and distinct tastes, a sweet and a bitter. The substance was made the subject of an investigation by Drs. Howell and Kastle, of the Johns Hopkins University, and, in a paper entitled "On the Nerves of Taste," it was by them shown that the nerves in the tip of the tongue are of a different character from those in the back part, and that to the former the substance is only sweet, while to the latter it is only bitter.

Dr. Kastle prepared para-chlor-sulphinide, also, in order to ascertain whether it has a similar effect upon the nerves of taste or not. It was found to possess both tastes in a more marked degree than did para-brom-sulphinide.

The object of this research was to investigate the other para-halogen-sulphinides, and the substances from which they were

[1] The previous papers in this series have appeared in This Journal **6**, 260; **8**, 223; **9**, 466.

[2] This investigation was undertaken at the suggestion of Professor Remsen, and I desire here to acknowledge my indebtedness to him for his valuable advice.

[3] This Journal **9**, 229.

made, and to observe their effect upon the nerves of taste. It was thought that some definite relation might be found to exist between the intensity of the taste and the chemical nature of the halogen contained in the sulphinide. Since para-brom-sulphinide was both sweet and bitter, and para-chlor-sulphinide was more sweet and more bitter, it seemed probable that para-fluor-sulphinide would be still more sweet and still more bitter, while para-iodo-sulphinide would not be either as sweet or as bitter as the brom-sulphinide. We should thus have a series:

Para-fluor-sulphinide, intensely SWEET and BITTER.
Para-chlor-sulphinide, strongly SWEET and BITTER.
Para-brom-sulphinide, moderately Sweet and Bitter.
Para-iodo-sulphinide, slightly sweet and bitter.

As regards this point, however, it may be at once stated that no such definite relation was found to exist, for para-fluor-sulphinide was almost purely sweet—fully as sweet as benzoic sulphinide—with only a very slightly bitter after-taste, and para-iodo-sulphinide had very little taste at all, and that was purely bitter; so that the series ran thus:

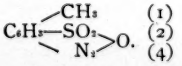
Para-fluor-sulphinide	= SWEET	.	bitter.
" chlor- "	= SWEET	.	BITTER.
" brom- "	= Sweet	.	BITTER.
" iodo- "	= ——	.	Bitter.

It therefore appears that no definite relation exists between the strength or chemical activity of the substituting halogen and the taste of the corresponding sulphinide.

The diazo compound which formed the starting-point in these investigations was made by starting with para-nitro-toluene, converting this into the ortho-sulphonic acid, which, by reduction with tin and hydrochloric acid, passes over into para-toluidine-ortho-sulphonic acid, from which the diazo compound was made.

Para-diazo-toluene-ortho-sulphonic Acid.

The starting-point in the preparation of the various compounds described in this paper was para-diazo-toluene-ortho-sulphonic acid[1] of the formula



[1]Ascher: Ann. Chem. (Liebig) **161**, 8.

This was made in the following manner: 50 grams of finely-powdered para-toluidine-ortho-sulphonic acid,[1] with 75 cc. of water, were made into a thin paste in a 500-cc. flask. The flask was placed in a bath of ice-water, and a rapid current of the gas from nitric acid and arsenic trioxide passed into it, the flask being constantly agitated. In from 10 to 15 minutes the contents of the flask had a frothy appearance, and granular crystals of the diazo compound had separated out. The current of gas was then stopped and the diazo compound almost completely precipitated as a heavy, granular mass, by the addition of about 300 cc. of alcohol. After agitating for a few minutes, this granular precipitate was rapidly filtered out with the aid of a pump, washed with alcohol, then with ether, and finally dried. In this manner, from 50 grams of para-toluidine-sulphonic acid 42 grams of pure-white diazo-toluene-sulphonic acid were obtained. On analysis—

I. 0.3973 gram gave 0.0555 gram nitrogen.

II. 0.3336 gram gave 0.0468 gram nitrogen.

		Found.	
	Calculated for $C_7H_6O_3N_2S$.	I.	II.
N	14.14	13.97	14.03

Para-fluor-toluene-ortho-sulphonic Acid.

This acid was prepared by decomposing diazo-toluene-sulphonic acid with hydrofluoric acid in the following manner:

About 500 cc. of concentrated hydrofluoric acid were slightly warmed in a large platinum dish and 100 grams of the diazo compound dissolved in it, the solution taking place with ease. This solution was heated until decomposition, accompanied by evolution of nitrogen, began. This decomposition was allowed to take place slowly, and when complete, the contents of the dish were evaporated to a syrupy consistency, diluted with about two liters of water in a large porcelain dish, heated, neutralised with precipitated chalk, boiled with animal-charcoal, and filtered. The filtered solution gave a blue color with ferric chloride, owing to the fact that some of the diazo compound had been converted into para-cresol-sulphonic acid by the action of the water of the hydrofluoric acid solution. The calcium salt of the para-fluor-toluene-sulphonic acid was not obtained well crystallised and sufficiently pure for analysis. The barium salt, however (prepared

[1] Brackett and Hayes: This Journal **9**, 400.

by neutralising with barium carbonate instead of precipitated chalk) was obtained in a very pure condition in small, glistening scales. It was recrystallised until its solution no longer gave a color with ferric chloride. When analysed—

I. 0.6160 gram, heated till constant weight, lost 0.0235 gram. 0.5925 gram dry salt gave 0.2704 gram $BaSO_4$.

II. 0.1090 gram, heated till constant weight, lost 0.0037 gram. 0.1053 gram dry salt gave 0.0477 gram $BaSO_4$.

	Calculated for $(C_7H_4O_3SF)_2Ba + H_2O$.	Found. I.	II.
H_2O	3.38	3.81	3 40
Ba	26.60	26.83	26.63

As a qualitative test for fluorine, a small quantity of the salt was mixed with lime and ignited in a platinum crucible, or fused with caustic potash in a silver crucible; dissolved in hydrochloric acid (treated with a little calcium chloride if the caustic potash method had been used) and neutralised with ammonia. A precipitate of calcium fluoride was thus obtained, which, when treated with sulphuric acid, produced an etching on a watch-glass. One of these tests was employed in each of the cases where fluorine compounds were made, and fluorine was found to be present in each.

Potassium fluor-toluene-sulphonate was made from the barium or the calcium salt by treating with potassium carbonate. It crystallised from concentrated aqueous solution in large, glistening scales, very soluble in water. It may be precipitated as a granular powder by adding alcohol to the concentrated aqueous solution. The salt contains two molecules of water of crystallisation. On analysis—

I. 50 grams, heated till constant weight, lost 6.8545 grams. 0.6570 gram dry salt gave 0.2493 gram K_2SO_4.

II. 0.2019 gram, heated till constant weight, lost 0.0274 gram. 0.1745 gram dry salt gave 0.0669 gram K_2SO_4.

	Calculated for $C_7H_4O_3SFK + 2H_2O$.	Found. I.	II.
H_2O	13.62	13.71	13.57
K	17.14	17.05	17.19

A qualitative test showed the presence of fluorine.

Para-chlor-toluene-ortho-sulphonic Acid.

This acid was prepared by decomposing diazo-toluene-sulphonic acid with hydrochloric acid, in the same way that the

fluor-toluene-sulphonic acid was made. Concentrated hydrochloric acid was used, and the product of decomposition was evaporated on the water-bath until very little odor of hydrochloric acid remained.

Barium chlor-toluene-sulphonate was made by diluting the syrupy residue with about three liters of water, neutralising with barium carbonate, boiling with animal-charcoal, filtering, and evaporating to crystallisation. The solution here, as in the case of the decomposition with hydrofluoric acid, gave a blue color with ferric chloride, due to the presence of the barium salt of para-cresol-sulphonic acid. The barium salt of para-chlor-toluene-sulphonic acid separated out in wart-like, amorphous, granular aggregates. It was recrystallised until a solution of the salt no longer gave a color with ferric chloride. The salt is very little more soluble in hot than in cold water. It contains one molecule of water of crystallisation.

I. 0.2190 gram, heated till constant weight, lost 0.0070 gram. 0.2120 gram dry salt gave 0.0528 gram $BaSO_4$.

II. 0.3714 gram, heated till constant weight, lost 0.0115 gram. 0.3599 gram dry salt gave 0.0905 gram $BaSO_4$.

	Calculated for $(C_7H_6O_3SCl)_2Ba + H_2O$.	Found. I.	II.
H_2O	3.18	3.20	3.09
Ba	25.04	24.91	25.17

This salt is identical with that prepared by Jenssen,[1] and Hübner and Majert.[2]

Potassium chlor-toluene-sulphonate was made from the barium salt by treatment with potassium carbonate. It crystallises from concentrated aqueous solution in light-yellow needles without water of crystallisation.

I. 0.3191 gram gave 0.1139 gram K_2SO_4.

II. 0.2220 gram gave 0.0798 gram K_2SO_4.

	Calculated for $C_7H_6O_3SClK$.	Found. I.	II.
K	15.95	16.00	16.11

Para-brom-toluene-ortho-sulphonic Acid.

This acid was prepared by adding gradually 100 grams of diazo-toluene-sulphonic acid to 200 grams of warm, concentrated

[1] Ann. Chem. (Liebig) **172**, 239. [2] Ber. d. chem. Ges. **6**, 793.

hydrobromic acid, and then heating till decomposition was complete.

Barium brom-toluene-sulphonate was prepared in the same manner as the corresponding chlor-toluene-sulphonate. It corresponded to the barium salt prepared by Jenssen,[1] and Hübner and Post.[2] The solution gave the color reaction with ferric chloride, showing that here also some cresol-sulphonic acid had been formed.

Potassium brom-toluene-sulphonate was made from the barium salt by treatment with potassium carbonate. This salt is not described by Hübner and Post.[3] It crystallises from the concentrated aqueous solution in thin, lustrous scales.

I. 0.2108 gram, heated till constant weight, lost 0.0122 gram.

II. 0.1986 gram dry salt gave 0.0598 gram K_2SO_4.

	Calculated for $C_7H_4O_3SBrK + H_2O$.	Found.
H_2O	5.86	5.79
K	13.50	13.50

Para-iodo-toluene-ortho-sulphonic Acid.

This acid was prepared by decomposing diazo-toluene-sulphonic acid with hydriodic acid in the following manner:

50 grams of the diazo compound were placed in a flask with 250 cc. of absolute alcohol, and 57 grams of concentrated hydriodic acid (57 per cent.) added in small portions, the flask being kept cool and being constantly agitated. When the evolution of nitrogen had ceased, the contents of the flask were gently warmed, in order to complete the decomposition, and the alcohol was then distilled off. The residue was diluted with five or six liters of water, heated, neutralised with lead oxide, and filtered while boiling-hot. The lead salt was very difficultly soluble, and could not be completely separated from the excess of lead oxide by repeated boiling with water. After being boiled two or three times with water, the residue was treated with a solution of potassium carbonate, which converted any undissolved lead salt into the potassium salt, which is easily soluble. The solution of the lead salt, upon cooling, becomes covered with an iridescent scum of a gummy consistency. If, however, the solution be evaporated to a small bulk, this scum gradually thickens as the boiling is continued, breaks up and

[1] Ann. Chem. (Liebig) **172**, 237. [2] Ibid. **169**, 15. [3] Ibid. **169**, 7.

falls to the bottom in heavy flakes, which can easily be separated. The mother-liquor, upon further evaporation, yielded another lead salt, which was very soluble. These lead salts were not themselves further investigated, but were converted into the better-crystallised potassium salts by treatment with potassium carbonate.

Potassium iodo-toluene-sulphonate was obtained from the difficultly-soluble lead salt through treatment with potassium carbonate. It crystallised from moderately-concentrated aqueous solution in transparent, whetstone-shaped crystals, corresponding to those of the potassium salt of the β-iodo-toluene-sulphonic acid described by Glassner.[1] The salt contains iodine, as was proved by a qualitative test, and crystallises with one molecule of water of crystallisation.

I. 0.3260 gram, heated till constant weight, lost 0.0169 gram. 0.3091 gram dry salt gave 0.0791 gram K_2SO_4.

II. 0.3090 gram, heated till constant weight, lost 0.0159 gram. 0.2931 gram dry salt gave 0.0721 gram K_2SO_4.

	Calculated for $C_7H_6O_3SIK + H_2O$.	Found. I.	II.
H_2O	5.08	5.18	5.14
K	11.61	11.11	11.03

The other potassium salt was much more soluble, and crystallised from concentrated aqueous solution in thin flakes. It did not contain iodine, but on analysis gave figures corresponding to the potassium salt of toluene-sulphonic acid.[2]

I. 0.1687 gram, heated till constant weight, lost 0.0132 gram. 0.1555 gram dry salt gave 0.0631 gram K_2SO_4.

II. 0.2865 gram, heated to constant weight, lost 0.0221 gram. 0.2644 gram dry salt gave 0.1090 gram K_2SO_4.

	Calculated for $C_7H_7O_3SK + H_2O$.	Found. I.	II.
H_2O	7.89	7.82	7.71
K	18.57	18.19	18.48

The toluene-sulphonic acid from which this salt was obtained was undoubtedly formed by the further action of hydriodic acid upon the para-iodo-toluene-sulphonic acid thus:

$$C_6H_3(CH_3)(SO_3OH)(I) + H \rightleftharpoons C_6H_3(CH_3)(SO_3OH)(H) + I_2$$

[1] Ber. d. chem. Ges. **8**, 561.

[2] Terry: Ann. Chem. (Liebig) **169**, 29.

The ease with which diazo-toluene-sulphonic acid is decomposed by the halogen acids increases as we pass from hydrofluoric to hydriodic acid.

The dry potassium salts of fluor-, chlor-, brom-, and iodo-toluene-sulphonic acids thus obtained, were treated, in turn, with phosphorus pentachloride and then with ammonia, thereby yielding the sulphon-chlorides and -amides. The details were as follows:

Para-fluor-toluene-sulphon-amide.

This was prepared by rubbing together in a dish 50 grams of anhydrous potassium fluor-toluene-sulphonate and 100 grams of phosphorus pentachloride; action taking place spontaneously and the mixture becoming hot and liquid. After driving off the greater part of the phosphorus oxychloride, and washing with cold water, the resulting sulphon-chloride, which was obtained as a slightly-yellow, viscous liquid, was allowed to drop slowly into a dish containing about a liter of strong aqueous ammonia. At first a bright-yellow solid was formed, which, after being broken up with a pestle and heated, went into solution. The solution was evaporated to dryness on the water-bath, the residue boiled with about 200 cc. of alcohol and a little animal-charcoal, filtered, and evaporated to crystallisation. The amide crystallises from the moderately-concentrated alcoholic solution in large, transparent, apparently orthorhombic, prisms terminated by dome-faces. It is easily soluble in alcohol and hot water, soluble with difficulty in cold water. From hot aqueous solution it crystallises in long, white needles. The melting-point is 155° (uncorrected).

I. 0.3137 gram gave 0.5093 gram CO_2 and 0.1242 gram H_2O.[1]
II. 0.2505 gram gave 0.4071 gram CO_2 and 0.0987 gram H_2O.
III. 0.5101 gram gave 0.0374 gram N (Kjeldahl).
IV. 0.1405 gram gave 0.1682 gram $BaSO_4$ (Carius).[2]
V. 0.0895 gram gave 0.1123 gram $BaSO_4$ (Carius).[2]
VI. 0.1053 gram gave 0.1306 gram $BaSO_4$ (Pearson).[2]
VII. 0.1899 gram gave 0.2358 gram $BaSO_4$ (Pearson).[2]

[1] The combustion-analyses of this, as well as those of the other compounds described in this paper, were made by a modified method devised by myself (*vide* This Journal **12**, 226). The method has been used with good results by several other students in this laboratory.

[2] These analyses were made by Mr. H. B. Skolfield, of the Johns Hopkins University.

	Calculated for $C_7H_8O_3NSF$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
C	44.44	44.28	44.32	...	...	...	...	...
H	4.23	4.40	4.38	...	...	...	...	...
N	7.41	...	...	7.33	...	...	...	...
S	16.93	...	...	...	16.44	17.23	17.03	17.05
F	10.06	...	...	...	...	...	...	...
O	16.93	...	...	...	...	...	...	...

A qualitative test showed the presence of fluorine.

Para-chlor-toluene-sulphon-amide.

This was made in exactly the same manner as the fluor-toluene-sulphon-amide. It is easily soluble in alcohol and in hot water; soluble with difficulty in cold water. It does not crystallise well from alcoholic solution; from aqueous solution it crystallises, on cooling, in long, white needles. The melting-point is 145° (uncorrected). This amide corresponds to that of Heffter.[1]

I. 0.2819 gram gave 0.4210 gram CO_2 and 0.1021 gram H_2O.
II. 0.3021 gram gave 0.4518 gram CO_2 and 0.1077 gram H_2O.
III. 0.5161 gram gave 0.0356 gram N (Kjeldahl).
IV. 0.4901 gram gave 0.0337 gram N (Kjeldahl).
V. 0.4026 gram gave 0.4530 gram $BaSO_4$ (Pearson).
VI. 0.2718 gram gave 0.3045 gram $BaSO_4$ (Pearson).
VII. 0.3456 gram gave 0.2392 gram AgCl (burning with lime).
VIII. 0.4387 gram gave 0.3031 gram AgCl (burning with lime).

	Calculated for $C_7H_8O_3NSCl$.	Found. I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	40.88	40.73	40.79	...	...	...	...	...	...
H	3.89	4.02	3.96	...	...	...	...	...	...
O	15.57	...	...	...	...	...	...	...	...
N	6.81	...	...	6.89	6.88	...	...	...	...
S	15.57	...	...	...	...	15.45	15.39	...	...
Cl	17.28	...	...	...	...	...	...	17.12	17.09

Para-brom-toluene-sulphon-amide.

This was made from potassium brom-toluene-sulphonate in the same manner as the corresponding fluor- and chlor-amides. This amide agreed with that prepared by Jenssen,[2] and Hübner and Post.[3]

[1] Ann. Chem. (Liebig) **221**, 209. [2] Ibid. **172**, 238. [3] Ibid. **169**, 15.

Para-iodo-toluene-sulphon-amide.

This was made by rubbing together in a dish 50 grams of anhydrous potassium iodo-toluene-sulphonate and 100 grams of phosphorus pentachloride. Action took place spontaneously, the mixture becoming hot and liquid. The resulting sulphon-chloride, after most of the phosphorus oxychloride had been driven off, was washed with cold water, and was thus obtained as a soft, white solid. When this was added to about a liter of strong aqueous ammonia, it did not all go into solution on boiling—as did the corresponding halogen compounds—but was nevertheless entirely converted into the amide. This amide is, therefore, not so soluble in ammonia as the others.

The contents of the dish were evaporated to dryness on the water-bath, boiled with about 200 cc. of alcohol and a little animal-charcoal, filtered, and evaporated to crystallisation. From the concentrated alcoholic solution the amide crystallises in fine, white needles. It is easy soluble in alcohol, sparingly soluble in hot water, from which on cooling it crystallises in white needles, finer than those from alcoholic solution. The melting-point is 185°–187° (uncorrected). This amide corresponds with the amide of the β-iodo-toluene-sulphonic acid prepared by Glassner.[1]

I. 0.1910 gram gave 0.2011 gram CO_2 and 0.0566 gram H_2O.

II. 0.2200 gram gave 0.2243 gram CO_2 and 0.0658 gram H_2O.

III. 0.5102 gram gave 0.02366 gram N (Kjeldahl).[2]

IV. 0.2080 gram gave 0.1641 gram AgI and 0.1640 gram $BaSO_4$ (Carius).

V. 0.2539 gram gave 0.2006 gram AgI and 0.2003 gram $BaSO_4$ (Carius).

	Calculated for $C_7H_6O_2NSI$.	Found. I.	II.	III.	IV.	V.
C	28.28	28.71	27.80	...	...	...
H	2.69	3.29	3.32	...	...	...
O	10.78	...	...	...	...	...
N	4.71	...	...	4.64	...	...
S	10.78	...	...	...	10.82	10.83
I	42.76	...	...	...	42.64	42.70

The Sulphinides.

These sulphon-amides, when oxidised by means of an alkaline solution of potassium permanganate, yielded, respectively, fluor-,

[1] Ber. d. chem. Ges. 8, 561.

[2] This analysis was made by Mr. C. E. Saunders.

chlor-, brom-, and iodo-sulphinide. The percentage of sulphinide obtained was in all cases considerably less than the theoretical yield, although the oxidation was conducted under a variety of conditions. The conditions under which the best yield of sulphinide was obtained—and this, irrespective of the substituting halogen —were found to be the following:

First of all, the amide to be oxidised must be free from foreign substances, as a small amount of the impurities which are liable to occur in the preparation of the amide greatly affects the result.

20 grams of the amide and 8 grams of caustic potash are dissolved in two liters of water in a large flask. The flask is placed in a bath of boiling water, and a concentrated solution of 35 grams of potassium permanganate added, a little at a time. The flask is kept in the bath of boiling water until all of the permanganate has been added, and only a slight pink color remains. This requires, as a rule, from 6 to 8 hours. A little alcohol is then added and the contents of the flask filtered, after which the residue is washed with hot water and the filtrate evaporated to about 75 cc. While still warm, the sulphinide, together with some unoxidised amide, is precipitated by the addition of an excess of strong hydrochloric acid. When cold, the liquid is filtered with the aid of a pump, and the sulphinide and amide on the filter are washed with a little cold water. In order to separate the unoxidised amide from the sulphinide, the mixture is boiled with water, neutralised with precipitated chalk, filtered, and allowed to cool, when the amide crystallises out in long, white needles, and can be separated. The solution, on further evaporation, yields the calcium salt of the sulphinide. The calcium salts of para-fluor-, para-chlor-, para-brom-, and para-iodo-sulphinide all crystallise from concentrated aqueous solution in radial groups of white needles. These salts have the same tastes as the sulphinides themselves.

The following results were obtained on analysing the four calcium salts:

Calcium Salt of Para-fluor-sulphinide.

I. 0.1876 gram, heated till constant weight, lost 0.0439 gram. 0.1437 gram dry salt gave 0.0446 gram $CaSO_4$.

II. 0.2037 gram, heated till constant weight, lost 0.0476 gram. 0.1561 gram dry salt gave 0.0488 gram $CaSO_4$.

	Calculated for $(C_7H_3O_3NSF)_2Ca + 7\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	23.48	23.40	23.37
Ca	9.09	9.13	9.19

Calcium Salt of Para-chlor-sulphinide.

I. 0.2514 gram, heated till constant weight, lost 0.0560 gram. 0.1954 gram dry salt gave 0.0553 gram $CaSO_4$.

II. 0.2515 gram, heated till constant weight, lost 0.0561 gram. 0.1954 gram dry salt gave 0.0565 gram $CaSO_4$.

	Calculated for $(C_7H_3O_3NSCl)_2Ca + 7\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	22.20	22.27	22.31
Ca	8.46	8.32	8.50

Calcium Salt of Para-brom-sulphinide.

This salt was prepared by Remsen and Bayley.[1] It gave figures corresponding to the formula $(C_7H_3O_3NSBr)_2Ca + 7\frac{1}{2}H_2O$.

Calcium Salt of Para-iodo-sulphinide.

I. 0.2575 gram, heated till constant weight, lost 0.0439 gram. 0.2136 gram dry salt gave 0.0440 gram $CaSO_4$.

II. 0.2482 gram, heated till constant weight, lost 0.0422 gram. 0.2060 gram dry salt gave 0.0421 gram $CaSO_4$.

	Calculated for $(C_7H_3O_3NSI)_2Ca + 7\frac{1}{2}H_2O$.	Found. I.	II.
H_2O	17.07	17.05	17.00
Ca	6.10	6.06	6.01

The sulphinides themselves were obtained as precipitates on adding hydrochloric acid to the saturated solutions of their respective calcium salts. They dissolve only with difficulty in cold water, and are even less soluble in hydrochloric acid.

Para-fluor-sulphinide.

This was obtained from its calcium salt by precipitation with hydrochloric acid, as stated above. It is moderately soluble in hot water, from which, on cooling, it crystallises in long, white needles which, on drying, break up into granules. When crystallised slowly from dilute solution it was obtained in small transparent rhombs. Its taste was almost purely sweet, but after

[1] This Journal **9**, 232.

remaining in the mouth for a few minutes a slightly-bitter after-taste was perceptible. This is also the case with benzoic sulphinide itself. As nearly as could be judged, its sweetness was fully as great as that of benzoic sulphinide. Its melting-point was 200°–202° (uncorrected).

I. 0.5086 gram gave 0.7772 gram CO_2 and 0.0971 gram H_2O.

II. 0.3980 gram gave 0.6080 gram CO_2 and 0.0746 gram H_2O.

III. 0.4873 gram gave 0.03346 gram nitrogen (Kjeldahl).

IV. 0.5008 gram gave 0.0347 gram nitrogen (Kjeldahl).

V. 0.3469 gram gave 0.3953 gram $BaSO_4$ (Pearson).

VI. 0.1856 gram gave 0.2096 gram $BaSO_4$ (Pearson).

	Calculated for $C_7H_4O_3NSF$.	Found. I.	II.	III.	IV.	V.	VI.
C	41.79	41.68	41.66	...	...	...	...
H	1.99	2.12	2.08	...	...	...	...
O	23.88	...	...	...	...	...	...
N	6.97	...	...	6.87	6.93	...	...
S	15.92	...	...	...	...	15.65	15.51
F	9.45	...	...	...	...	...	...

A qualitative test proved the presence of fluorine.

Para-chlor-sulphinide.

This also was obtained from its calcium salt by precipitation with hydrochloric acid. It is not quite so soluble as para-fluor-sulphinide. It crystallises from aqueous solution in thin, pearly scales. The melting-point is 218° (uncorrected). It has both a sweet and a bitter taste. Both tastes are very marked, but the bitter seems to be the more intense of the two. This substance was prepared in small quantity by Dr. Kastle when at the Johns Hopkins University, in order to ascertain its effect upon the nerves of taste. It was not further studied by him, and its preparation was not put on record. I have obtained, on analysis, the following figures:

I. 0.4416 gram gave 0.6234 gram CO_2 and 0.0799 gram H_2O.

II. 0.5671 gram gave 0.8021 gram CO_2 and 0.0972 gram H_2O.

III. 0.3125 gram gave 0.4414 gram CO_2 and 0.0561 gram H_2O.

IV. 1.0000 gram gave 61 cc. nitrogen at 25° and 738 mm. (Dumas).

V. 1.0000 gram gave 60 cc. nitrogen at 25° and 736 mm. (Dumas).

VI. 1.0000 gram gave 60.6 cc. nitrogen at 25° and 734 mm. (Dumas).

VII. 0.7000 gram gave 0.04445 gram nitrogen (Kjeldahl).[1]

VIII. 0.7000 gram gave 0.0448 gram nitrogen (Kjeldahl).[1]

IX. 0.5113 gram gave 0.5497 gram $BaSO_4$ (Pearson).[2]

X. 0.3894 gram gave 0.4192 gram $BaSO_4$ (Pearson).[2]

XI. 1.0121 gram gave 0.6732 gram AgCl (burning with lime).

XII. 1.0006 gram gave 0.6603 gram AgCl (burning with lime).

XIII. 0.2141 gram gave 0.1414 gram AgCl (Carius).[3]

	Calculated for $C_7H_4O_3NSCl$.	Found. I.	II.	III.	IV.	V.	VI.
C	38.62	38.50	38.57	38.52	...	...	...
H	1.84	2.01	1.90	1.99	...	...	...
O	22.07	...	...	...	...	...	...
N	6.44	...	...	...	6.60	6.47	6.52
S	14.71	...	...	...	...	...	...
Cl	16.32	...	...	...	...	...	...

	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
C	...	...	...	...	...	...	...
H	...	...	...	...	...	...	...
O	...	...	...	...	...	...	...
N	6.35	6.40	...	...	...	...	...
S	...	...	14.77	14.79	...	...	...
Cl	...	...	...	...	16.45	16.33	16.34

Para-brom-sulphinide.

This was made from its calcium salt by precipitation with hydrochloric acid. It was slightly less soluble than para-chlor-sulphinide. Its properties corresponded in all respects with those of the substance prepared by Remsen and Bayley.[4] It possesses both tastes, but in a less marked degree than para-chlor-sulphinide. The yield obtained by conducting the oxidation of the sulphon-amide under the previously-mentioned conditions, was larger than was obtained by Remsen and Bayley. The yield was 10–12 per cent. of the theoretical.

[1] These analyses were made by Dr. A. M. Peter, Ky. Ag. Exp. Sta.
[2] These analyses were made by Dr. J. H. Holmes, J. H. U.
[3] This analysis was made by Mr. B. C. Hinde, J. H. U.
[4] This Journal **9**, 229.

Para-iodo-sulphinide.

This, too, was obtained from its calcium salt by precipitation with hydrochloric acid. It is the least soluble of the halogen sulphinides. It crystallises from hot aqueous solution, on cooling, in fine, white needles. Its melting-point is 230°–232° (uncorrected). Its taste is not very marked, being only slightly bitter; there is no sweet taste whatever.

I. 0.3440 gram gave 0.3441 gram CO_2 and 0.0414 gram H_2O.

II. 0.2624 gram gave 0.2632 gram CO_2 and 0.0324 gram H_2O.

III. 0.2877 gram gave 0.2883 gram CO_2 and 0.0361 gram H_2O.

IV. 0.6132 gram gave 0.0273 gram nitrogen (Kjeldahl).

V. 0.7017 gram gave 0.0309 gram nitrogen (Kjeldahl).

VI. 0.1819 gram gave 0.1390 gram AgI and 0.1387 gram $BaSO_4$ (Carius).

VII. 0.2327 gram gave 0.1776 gram AgI and 0.1769 gram $BaSO_4$ (Carius).

	Calculated for $C_7H_4O_3NSI$.	Found. I.	II.	III.	IV.	V.	VI.	VII.
C	27.185	27.28	27.35	27.33	...	...	...	...
H	1.295	1.34	1.37	1.39	...	...	...	...
O	15.53	...	...	...	...	...	...	...
N	4.53	...	...	...	4.45	4.40	...	...
S	10.36	...	...	...	...	...	10.45	10.44
I	41.10	...	...	...	...	...	41.29	41.25

Acid Ammonium Para-chlor-ortho-sulpho-benzoate.

It is well known that, when boiled with dilute hydrochloric acid, benzoic sulphinide is converted into the acid ammonium salt of ortho-sulpho-benzoic acid.[1] It was thought very probable that under the same treatment the para-halogen-sulphinides would behave in the same manner. This was found to be the case with para-chlor-sulphinide. The other halogen sulphinides were not investigated with regard to this point. They would probably act in the same way.

5 grams of para-chlor-sulphinide were boiled with dilute hydrochloric acid for about an hour, the flask being connected with a reflux-condenser. The contents of the flask were then evaporated to dryness, and heated on the water-bath until all odor of hydro-

[1] Remsen and Burton: This Journal **11**, 404.

chloric acid had disappeared. The residue was dissolved in water, in which it was easily soluble. The solution had no taste, and on slow evaporation gave crystals similar in appearance to the acid ammonium salt of sulpho-benzoic acid. It was shown by analysis to be acid ammonium para-chlor-ortho-sulpho-benzoate.

I. 0.5372 gram gave 0.0359 gram NH_3.

II. 0.4896 gram gave 0.0321 gram NH_3.

	Calculated for $C_6H_3(\overset{(1)}{COOH})(\overset{(2)}{SO_2O.NH_4})(\overset{(4)}{Cl})$.	Found. I.	Found. II.
NH_3	6.71	6.68	6.56

While then the tastes of the halogen-derivatives of benzoic sulphinide differ markedly from one another, it is, as will be seen, a difficult matter to describe these differences accurately. The relative degrees of sweetness and bitterness can, of course, be only roughly measured. It is also impossible to make accurate comparison between a sweet and a bitter taste as regards the relative intensity of the two. There is also a difference of opinion amongst those who have tasted these substances. The majority, however, were of the opinion that the substances have the tastes described in the preceding pages.

ON THE COMPOSITION OF CERTAIN PETROLEUM OILS, AND OF REFINING-RESIDUES.[1]

By Charles F. Mabery.

In an examination of crude Lima oil that I had occasion to make in the early development of the Ohio oil fields in 1885, I observed the peculiar, penetrating odor of the sulphur compounds; and while they were present in all fractions during distillation, I noted that they collected principally in the portions with higher boiling-points (between 200° and 300°). A systematic examination of the oil was soon undertaken for the purpose of ascertaining

[1] From the Proceedings of the American Academy of Arts and Sciences, Vol. 25 (December, 1890). Communicated by the Author.

the form of the sulphur compounds: but little had been accomplished when the work was interrupted by a destructive fire, and it was not resumed until two years later.

In published accounts of the composition of petroleum oils I have found very few allusions to the presence of sulphur, and those that appear are limited to the products of distillation. Hagar[1] found carbonic disulphide in petroleum-ether, but none in burning-oil. H. Vohl[2] reported sulphur in considerable quantities as sulphuric acid in numerous samples of crude (Roh) petroleum. But from the data given and allusions to the products as burning-oils, they had undoubtedly been refined with the aid of sulphuric acid. Much difficulty has been experienced in the removal of sulphur from the distillates of Ohio oil, and consequently few, if any, of the commercial products are entirely free from sulphur, while it is frequently present in considerable quantities.

This paper contains a description of results thus-far obtained, of which the following is a summary:—

1. The separation and identification of methyl, ethyl, normal propyl, iso- and normal butyl, pentyl, ethyl-pentyl, and hexyl sulphides, which are present in crude Ohio petroleum.

2. The separation of certain sulphides that do not correspond in boiling-points nor in composition with any sulphides hitherto described: these will be further examined.

3. The separation of certain sulphur-free oils, apparently unsaturated, that also require further study.

I am not aware that these alkyl sulphides have hitherto been identified as natural products.

I. THE SULPHUR COMPOUNDS IN OHIO PETROLEUM.

By Charles F. Mabery and Albert W. Smith.

When the various distillates from Ohio oils are agitated with concentrated sulphuric acid, the sulphur compounds are partially removed in combination with the acid. By neutralising the acid solution with plumbic carbonate, filtering, and evaporating carefully, lead salts, soluble in water, are obtained that are easily decomposed by heat with the formation of plumbic sulphide. If the acid solution be neutralised with calcic carbonate or calcic hydrate,

[1] Jahresb. Liebig, 1867, p. 947, Aus. Pharm. Centrbl.
[2] Ibid., 1875, p. 1053; Dingl. Journal **216**, 47.

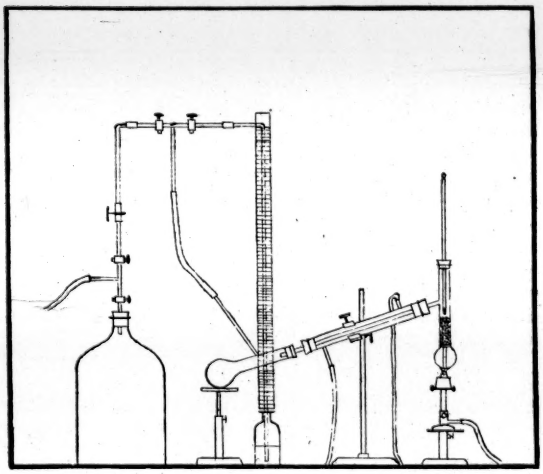
unstable calcium salts are formed that are readily decomposed by distillation with steam, which carries over the sulphides without decomposition.

In applying, for the separation of the sulphur compounds from the crude oil, a method based upon these observations, we procured fifty liters of what is technically known as sludge-acid, that had recently been used in refining Lima burning-oil, and, after dilution, we neutralised it in the cold with slaked lime and distilled the mixture of solution and solid with steam. We thus obtained 2270 grams of the sulphur-oil that was colorless when freshly distilled, and entirely free from hydric sulphide. Analysis showed that it contained 14.97 per cent. of sulphur with a specific gravity at 16.5° of 0.9245. Analyses of samples of crude Ohio oils from different localities have given on the average about 0.50 per cent. of sulphur.

Distillation of the oil with steam under atmospheric pressure produced such serious decomposition that we were forced to conduct all fractional separations with diminished pressure; but since the decomposition was inappreciable at tensions reduced to 150 mm., this involved but little additional labor, except in the inconvenience of maintaining the required tensions with the use of common corks without lutings, which became necessary on account of the solvent action of the oil. The fractional distillations were carried on in the apparatus represented in the accompanying diagram; while it contains no features not hitherto described, it may serve to illustrate how such an apparatus to work satisfactorily can readily be arranged from material always at hand in the laboratory.

Hill's[1] application of the Hempel device, which consists in supporting glass beads in the neck of the distillation-flask on a piece of glass rod with one end enlarged, is a means of saving much time in a long series of separations. The receiver is simply a second distillation-flask. This form of manometer was most convenient, since hydric sulphide was evolved to a certain extent, and, the manometer-tube becoming discolored by mercuric sulphide, occasionally it had to be cleaned. In exhausting the apparatus we used an ordinary glass water-pump, and to avoid loss of time in disconnecting the flask, a ten-liter bottle was inserted as a reservoir, with the stopcocks necessary for continuous action, and

[1] Proc. Am. Acad. 24, 342.



a nipper-tap with an enlarged thumbscrew was also attached for closely adjusting the pressure.[1] With this apparatus there is scarcely more interruption to continuous distillation than at atmospheric pressure. From 1000 grams of the oil at the end of the sixth distillation, with a tension of 150 mm., the following weights were obtained:

Temperatures,	—70°	70–80°	80–90°	90–95°	95–100°	100–105°
Grams,	12	8.5	16	16	26	20.5
Temperatures,	105–110°	110–115°	115–120°	120–125°	125–130°	130–135°
Grams,	31	30	83	47.5	59	66
Temperatures,	135–140°	140–145°	145–150°	150–155°	155–160°	160°+
Grams,	69	56.5	75	36	40.5	230

Total, ... 921.5

At the end of the twenty-second distillation, with the tension reduced to 100 mm., the products collected, to a large extent, within well-defined limits of temperature and several determinations of sulphur gave the following results:

[1] We were unable to use the convenient device of Anschütz for maintaining constant tensions, since the current of air produced considerable decomposition of the oils.

Fraction,	—76°	80–90°	98–101°	135–145°	148–155°	185–200°
Per cent. sulphur,	2.60	7.34	18.23	15.52	16.44	14.21

All fractions containing sulphur gave, with alcoholic, and with aqueous mercuric chloride, precipitates which were either crystalline, or, with the less-volatile products, thick, viscous oils. The latter usually became solid on standing, or when crystallised from benzene. As a qualitative test for sulphur, we depended upon the exceedingly delicate nitro-prussid reaction, which was especially serviceable in separating sulphur-oils from those containing no sulphur. The platinum compounds R_2SPtCl_4 were readily formed with chlor-platinic acid with evolution of hydrochloric acid. With bromine all fractions united with great energy with the formation of oils heavier than water. These reactions suggested the presence of sulphides, or with sulphur-free oils the reaction with bromine indicated unsaturated hydrocarbons.

When distilled at temperatures above 140°, under atmospheric pressure, the oils became thick and dark in color, and hydric sulphide was freely evolved. Since at lower temperatures the decomposition was slight, the fractional separation of the products collected below 101° (P = 100 mm.—see above) was carried further. The products thus collected below 125°, united readily with concentrated hydrobromic acid when heated, forming oils heavier than water. The fraction 80°–90° was nearly all converted into the heavy addition-product, and the fraction 90°–100° separated into two products, one heavier and one lighter than water, the latter in somewhat smaller quantity than the former. The addition-product from the fraction 80°–90° possessed the characteristic odor of the substituted paraffin hydrocarbons, and upon analysis it gave a percentage of bromine corresponding to that required for monobrom-heptylene:

0.1850 gram of the substance gave 0.1116 gram AgBr.

	Calculated for $C_7H_{15}Br$.	Found.
Br	46.93	46.57

With bromine this product united with a violent reaction, and the resulting oil gave the percentage of bromine required for dibrom-heptylene:

0.1938 gram of the substance gave 0.2797 gram AgBr.

	Calculated for $C_7H_{14}Br_2$.	Found.
Br	62.01	61.42

This fraction therefore consists principally of a heptylene probably identical with that obtained by Pelletier and Walthier from the coal-oil of Amiano.[1]

Upon the addition of alcoholic mercuric chloride to fraction 110°–125° (atmospheric pressure), a fine, crystalline precipitate was formed that contained the percentage of mercury required for methyl sulphide:

0.3156 gram of the mercury compound gave 0.2214 gram HgS.

	Calculated for $(CH_3)_2S.HgCl_2$.	Found.
Hg	60.06	60.47

The fraction 125°–135° also gave a crystalline precipitate with alcoholic mercuric chloride, which after crystallisation from benzene gave a percentage of mercury corresponding to ethyl sulphide:

0.5056 gram of the mercury compound gave 0.3122 gram HgS.

	Required for $(C_2H_5)_2S.HgCl_2$.	Found.
Hg	55.40	55.42

Although the boiling-points of the oils from which these mercury addition-products were separated, were considerably higher than those of the sulphides to which the mercury-determinations correspond, these oils consisted to a certain extent of hydrocarbons which were subsequently found to contain no sulphur. The higher fractions gave, with mercuric chloride, oily addition-products which became crystalline after washing with alcohol, and separation from hot benzene. The addition-product from fraction 150°–155° gave 53.33 per cent. Hg; calculated for $(C_3H_7)_2SHgCl_2$, 51.41 per cent. Hg. It was therefore probably a mixture of propyl and butyl sulphides. From fraction 155°–160° the addition-product with mercuric chloride gave upon analysis 49.44 per cent. Hg; required for $(C_4H_9)_2SHgCl_2$, 47.96 per cent. Hg. It therefore still contained a lower sulphide. On account of the small quantity of these products obtained, we were unable to separate them more completely.

We will next describe in detail the separation of the various sulphides.—

Methyl Sulphide.

Further attempts were made to separate the lower sulphides from the crude naphtha distillate. We procured from Findley oil 250 liters of crude naphtha that nearly all distilled below 150°,

[1] Berzelius' Jsb. **21**, 470.

and agitated it thoroughly in quantities of five liters each, with aqueous mercuric chloride. The heavy, flocculent precipitate that separated was subjected to heavy pressure in a screw press, dried, and decomposed by hydric sulphide in presence of alcohol. For the decomposition of considerable quantities of the mercury addition-product, vigorous agitation was necessary, and the mercuric sulphide invariably separated in the form of the red modification. After filtration, the alcoholic solution of the oil was diluted with water, the oil collected in a separatory funnel, washed, dried, and submitted to fractional distillation. It was nearly colorless, with a specific gravity of 0.8543 at 20°. Distilled under atmospheric pressure the decomposition was less marked than in the case of the oil extracted with sulphuric acid. A small quantity of the oil was collected below 50° that gave a percentage of sulphur corresponding to methyl sulphide—

0.1800 gram of the oil gave by the method of Carius 0.6672 gram $BaSO_4$.

	Calculated for $(CH_3)_2S$.	Found.
S	51.61	50.89

Between 60° and 80° the quantity of distillate was too small to prove the presence of methyl-ethyl sulphide. Results of analysis were intermediate between the requirements for methyl and ethyl sulphides, but not sufficiently close for methyl-ethyl sulphide. On account of the great amount of labor involved in the separation of these volatile oils, no further attempts were made to identify this sulphide, especially as its presence was regarded as doubtful.

Ethyl Sulphide.

After long-continued fractional distillations, we succeeded in obtaining a product distilling between 88° and 92° that gave a percentage of sulphur corresponding to ethyl sulphide—

0.1632 gram of the oil gave 0.4183 gram $BaSO_4$.

	Calculated for $(C_2H_5)_2S$.	Found.
S	35.55	34.86

Ethyl-propyl Sulphide.

At several points between 91° and 130°, the boiling-points respectively of ethyl and propyl sulphides, distillates collected in considerable quantities. A fraction that distilled at 110°–112°

contained the percentage of sulphur required for ethyl-propyl sulphide—

0.2445 gram of the substance gave 0.5396 gram $BaSO_4$.

	Calculated for $\left\{\begin{matrix}C_2H_5\\C_3H_7\end{matrix}\right\}S$.	Found.
S	30.77	30.31

The platinum salt was formed by the addition of alcoholic chlor-platinic acid, and it gave on analysis the required percentage of platinum—

0.3240 gram of the substance gave 0.1158 gram Pt.

	Calculated for $[(C_2H_5.C_3H_7)S]_2.PtCl_4$.	Found.
Pt	36.01	35.75

The quantity of this sulphide obtained was insufficient for complete examination, and further study of it, as well as of other fractions of low boiling-points, must therefore be postponed until we can secure a larger supply of material.

Normal Propyl Sulphide.

All attempts to isolate iso-propyl sulphide were unsuccessful; very little of the distillate collected between 115° and 125°, and analysis showed that it could not be the iso-propyl compound that boils at 120°. The fraction 115°–120° gave 29.29 per cent. S, and the fraction 120°–125°, 28.52 per cent. S; calculated for $(C_3H_7)_2S$, 27.12 per cent. S. Analysis of platinum salts of these fractions gave similar results. Normal propyl sulphide was readily identified in the fraction 127°–132°, which collected in larger quantities—

0.0443 gram of the substance gave 0.0880 gram $BaSO_4$.

	Calculated for $(C_3H_7)_2S$.	Found.
S	27.12	27.44

The presence of propyl sulphide was further shown by analysis of the platinum salt—

I. 0.1720 gram of the salt gave 0.0600 gram Pt.

II. 0.1309 gram of the salt gave 0.0457 gram Pt.

III. 0.0930 gram of the salt gave 0.0329 gram Pt.

	Calculated for $[(C_3H_7)_2S]_2.PtCl_4$.	Found. I.	Found. II.	Found. III.
Pt	34.26	34.10	34.92	35.15

Analyses II and III were made of preparations from fraction 80°–90° (P = 150 mm.) that were obtained in fractioning the oil

from the sulphuric-acid extract. This oil contained only very small quantities of propyl sulphide, or of its lower homologues. It consisted mainly of higher sulphides and of sulphur-free oils. The presence of heptylene has been described, and nearly all fractions contained sulphur-free oils that united readily with bromine, and those of lower boiling-points with hydrobromic acid. The sulphides were separated by dissolving the oil in alcohol, and adding a small excess of alcoholic mercuric chloride. An aqueous solution precipitates the sulphides, but it is apt to carry down the sulphur-free oil. The precipitates were usually in the form of a thick, viscous mass, although with care they could be obtained crystalline. They were washed with alcohol, and decomposed with hydric sulphide in presence of alcohol. The filtered alcoholic solution was diluted with water, and the sulphide that separated was washed free from hydric sulphide, dried, and again submitted to fractional distillation for analysis.

Upon dilution of the alcohol from the precipitation by mercuric chloride, an oil separates that is lighter than water, and possesses an exceedingly disagreeable odor. These oils unite readily with bromine and with hydrobromic acid, and they contain no sulphur. Whether they are decomposition-products resulting from the action of sulphuric acid upon the sulphur-oils, or are normal constituents of the crude petroleum, we have not fully determined. But since the sludge-acid showed very little indication of decomposition, it seems probable that the sulphur-free oils are abstracted by sulphuric acid during the process of refining.

The composition of the fractioned sulphides before and after treatment with mercuric chloride may be shown by the effect on the percentage of sulphur. The fraction 135°–140° (P = 150 mm.; B. P. = 185°–190°, P normal) gave 15.40 per cent. S. After treatment with mercuric chloride as described above, analysis showed 20.37 per cent. S.

The higher sulphides were all obtained from fractions of the oil that was extracted from sludge-acid. Those of medium boiling-points may be separated in smaller quantities from naphtha-distillates by mercuric chloride, which has the advantage that the sulphides are uncontaminated by other products. But this method is exceedingly laborious, and the yields are small. We have in mind a modification that works successfully with small quantities of the mercury addition-product. It includes recovery of the mercury by conversion of the sulphide into the sulphoxide.

Ethyl-pentyl Sulphide.

After the twenty-second distillation (page 235) from fraction 95°–100° (P = 100 mm.), a sulphide was obtained, through the mercury compound, that distilled without decomposition at 156°–160°. It gave, upon analysis, the percentage of sulphur required for ethyl-pentyl sulphide (B. P. 158°–159°).

I. 0.2629 gram of the oil gave 0.4516 gram $BaSO_4$.

II. 0.1169 gram of the oil gave 0.2056 gram $BaSO_4$.

	Calculated for $\left.\begin{matrix}C_2H_5\\C_5H_{11}\end{matrix}\right\}S$.	Found. I.	II.
S	24.24	23.59	24.15

Iso-butyl Sulphide.

The mercury addition-product from fraction 110°–115° (P = 100 mm.) was decomposed with hydric sulphide, and the alcoholic solution diluted with water. After drying over calcic chloride, the oil, thus obtained, distilled at 170°–176°, which corresponded to the boiling-point of iso-butyl sulphide (172°), and its composition was further shown by a determination of sulphur—

0.1750 gram of the oil gave 0.2760 gram $BaSO_4$.

	Calculated for $(C_4H_9)_2S$.	Found.
S	21.92	21.66

Normal Butyl Sulphide.

The fraction 117°–125° (P = 100 mm.) gave an addition-product with mercuric chloride from which an oil was obtained that distilled at 180°–185° (B. P. of normal butyl sulphide = 182°), and the percentage of sulphur indicated butyl sulphide—

I. 0.1633 gram of the oil gave 0.2657 gram $BaSO_4$.

II. 0.2929 gram of the oil gave 0.3236 gram $BaSO_4$.

	Calculated for $(C_4H_9)_2S$.	Found. I.	II.
S	21.92	22.35	21.07

Butyl-pentyl Sulphide.

An inspection of the weights of distillate collected at different temperatures given on page 235 will show a tendency of the distillates to collect at certain temperatures, and this is especially evident in the fraction 135°–140°. As the distillation proceeded, the fractions at these points increased in quantity, and, so far as

examined, each of them corresponded to a definite sulphide. From the fraction 135°–140°, by decomposition of the addition-product with mercuric chloride, an oil was obtained that distilled at 185°–190° (Bar. = 740 mm.), and the percentage of sulphur corresponded to butyl-pentyl sulphide—

I. 0.2509 gram of the oil gave 0.3721 gram $BaSO_4$.

II. 0.2676 gram of the oil gave 0.3925 gram $BaSO_4$.

	Calculated for $\left\{\begin{matrix}C_4H_9\\C_5H_{11}\end{matrix}\right\}S$.	Found. I.	II.
S	20.00	20.37	20.14

It is hardly probable that this product was a mixture of butyl and pentyl sulphides, since it was obtained at different times after prolonged distillation. It will be further examined.

Pentyl Sulphide.

This sulphide was separated from the fraction 150°–155° (P = 100 mm.) by conversion into the mercury compound, and decomposition with hydric sulphide. Different preparations from independent fractions distilled, with very little decomposition, at 205°–210° (Bar. = 745.5 mm.), which is somewhat lower than the boiling-point assigned to pentyl sulphide (216°). But from the results of analysis there can be no doubt as to the composition of this sulphide—

I. 0.1987 gram of the oil gave 0.2717 gram $BaSO_4$.

II. 0.2723 gram of the oil gave 0.3716 gram $BaSO_4$.

III. 0.2844 gram of the oil gave 0.3902 gram $BaSO_4$.

	Calculated for $(C_5H_{11})_2S$.	Found. I.	II.	III.
S	18.39	18.75	18.74	18.85

It is quite probable that the low boiling-point was due to the presence of a very small quantity of a lower sulphide, since the sulphur-determinations are somewhat higher than the percentage required for pentyl sulphide.

Hexyl Sulphide.

From the fraction 160°–170° (P = 100 mm.), by precipitation with mercuric chloride and decomposition with hydric sulphide, a light-yellow oil was obtained that distilled with some decomposition at 225°–235°, and gave the percentage of sulphur required for hexyl sulphide—

0.3110 gram of the oil gave 0.3531 gram $BaSO_4$.

	Calculated for $(C_6H_{13})_2S$.	Found.
S	15.84	15.59

At least one-third of the original oil distilled above the boiling-point of hexyl sulphide, but with considerable decomposition, even under diminished pressure. It consisted to a very large extent of sulphides, but we have not attempted to separate them for identification.

In order to overcome any doubt that these sulphides are contained in the crude petroleum, we distilled several liters under diminished pressure (to avoid decomposition), and extracted portions of various distillates with sulphuric acid, and other portions with aqueous mercuric chloride. The oils, separated from the acid solution and from the mercuric chloride addition-product, resembled in all respects the products previously described. From the distillate corresponding to 150°–300° (atmospheric pressure), or to the best grades of burning-oil, by agitation with aqueous mercuric chloride, the characteristic heavy precipitate was formed, and the oil obtained from it contained 19.72 per cent. sulphur and gave all the reactions for sulphides. In separating sulphides from oils extracted with sulphuric acid, we have frequently obtained small quantities of a product with a penetrating odor resembling that of turpentine; and, at other times, oils containing no sulphur, but with an odor characteristic of certain ethereal oils, such as peppermint or pennyroyal. We have not yet obtained these oils in quantity sufficient for examination.

The study of Ohio oils will be continued, and the investigation will include an examination of oils from other localities, for sulphur compounds, and also of the composition of other acid-residues and by-products obtained in refining petroleum oils.

Chemical Laboratory, Case School of Applied Science.

ON THE ACTION OF PHOSPHORUS OXYCHLORIDE ON THE ETHERS AND CHLORHYDRINES OF SILICIC ACID.

By H. N. Stokes.

That silica can combine with other acids, forming mixed anhydrides, has long been known, and several such bodies have been described. Friedel and Ladenburg[1] obtained the tetra-acetyl derivative $Si(O.CO.CH_3)_4$ by treating silicon tetrachloride with acetic acid or anhydride. Friedel and Crafts[2] obtained $Si(OC_2H_5)_3O.CO.CH_3$ from ethyl orthosilicate and acetic anhydride. Hautefeuille and Margottet[3] described a crystalline compound, $SiO_2.P_2O_5$, formed by fusing amorphous silica with metaphosphoric acid.

By the action of phosphorus oxychloride on silicic ethers and their chlorine derivatives, I have obtained bodies which consist of phosphoryl chlorides in which the chlorine is partly replaced by a residue of silicic acid, and which are therefore chlorides of silicophosphoric acids.

Phosphorus oxychloride was caused to react upon *orthosilicic ethyl-trichlorhydrine*, $SiCl_3.OC_2H_5$, hoping thereby to obtain the silicon oxychloride described by Friedel and Ladenburg[4] and by Troost and Hautefeuille[5]:

$$3SiCl_3.OC_2H_5 + POCl_3 = (SiCl_3O)_3PO + 3C_2H_5Cl,$$

and

$$2(SiCl_3O)_3PO = 3Si_2OCl_6 + P_2O_5.$$

The experiment proved that this reaction does not take place.

If the trichlorhydrine be heated in a sealed tube with an excess of phosphorus oxychloride, no reaction is apparent below 175°, the contents remaining perfectly clear. If the temperature be kept at 180°–200°, a white, amorphous substance is soon formed which is sufficiently porous to absorb all the liquid products. After 2–3 hours' heating the tube is opened, when ethyl chloride escapes in large quantities. On placing the tube in an air-bath heated at about 150°, and connecting it with a condenser, a large amount of liquid may be collected. The solid remaining in the

[1] Ann. Chem. (Liebig) **146**, 174.
[2] Ann. chim. phys. [4] **9**, 47.
[3] Compt. rend, **96**, 1052.
[4] Ann. Chem. (Liebig) **147**, 355.
[5] Ann. chim. phys. [5] 7, 465.

tube may then be freed from excess of phosphorus oxychloride by passing a current of dry air over it by means of a capillary.

The liquid, on fractioning, is readily separated into phosphorus oxychloride (boiling at 110°) and silicon tetrachloride (boiling at 57°–61°), though much of the latter is lost, being carried off by the ethyl chloride which is abundantly held in solution. The product obtained after six distillations was analysed.

	Calculated for $SiCl_4$.	Found.
Si	16.52	16.24

The view with regard to its nature was confirmed by converting it into ethyl orthosilicate (boiling at 165.5°). As the liquid passed over entirely below 112°, no silicon oxychloride was formed, and no substances other than those mentioned could be detected.

Analyses of the solid substance gave :

	Calculated for $SiP_2O_6Cl_2$.	Found. I.	Found. II.
Si	10.92	10.17	10.06
P	24.15	25.16	25.11
Cl	27.59	27.33	...

The agreement is only approximate, as the substance could not be purified in any way ; and on heating too long or at too high a temperature, when drying, phosphorus oxychloride is slowly given off. It is possibly a mixture of substances, in the formation of which the one supposed represents one stage. If heated above 200° phosphorus oxychloride is given off, and, at a red heat, phosphorus pentoxide ; and the residue left at a white heat consists of amorphous silica imbedded in a vitreous substance, probably the compound $SiO_2.P_2O_5$ of Hautefeuille and Margottet. The loss on heating corresponds to the equation—

$$6SiP_2O_6Cl_2 = 3SiO_2 + 3(SiO_2.P_2O_5) + 4POCl_3 + P_2O_5.$$

	Calculated.	Found.
Loss,	49.01	51.86

The formation of the substance, which, for reasons given below, may be designated as *silico-pyrophosphoryl chloride*, is most simply expressed by the equation—

$$4SiCl_3(OC_2H_5) + 2POCl_3 = 3SiCl_4 + SiP_2O_6Cl_2 + 4C_2H_5Cl.$$

Silico-pyrophosphoryl chloride is a very bulky substance, resembling the lightest form of amorphous silica. It may be

obtained perfectly colorless, but is usually more or less colored by organic matter, formed by secondary reactions, when heated too high. It is extremely hygroscopic, and gives off hydrochloric acid instantly when exposed to moist air. It is readily soluble in absolute alcohol—a proof that it contains no free silica. The alcoholic solution, which probably contains an ether of silico-phosphoric acid, may be evaporated nearly to dryness, or heated any length of time at 150° without decomposition. On heating at 225° it soon deposits transparent, gelatinous silica. The solution in alcohol is attended with considerable rise of temperature. The substance is insoluble in ether. If cold water be poured on the fine powder it readily dissolves, with the exception of a few flakes of silica; but if first moistened, or if in lumps, most of the silica remains undissolved: the best way to get a clear aqueous solution is to dissolve in a little alcohol and then to dilute with water. The reaction with water alone is somewhat violent. The aqueous solution may be kept a long time—indeed, may be strongly concentrated on the water-bath—but on evaporation *to dryness* a vitreous mass is left, from which water extracts phosphoric acid only.

All attempts to prepare salts of silico-phosphoric acid have failed. Ammonium carbonate precipitates gelatinous silica. If the cold aqueous solution, prepared as described above, be acidified with nitric acid, excess of silver nitrate added, and filtered from silver chloride, a clear solution is obtained. If to this be added, drop by drop, dilute ammonia, a white precipitate is formed, which at a certain point changes to yellow. The analysis of the white substance (dried at 100°) gave—

	Calculated for $Ag_4P_2O_7$.	Found.
Ag	71.17	71.25

The yellow precipitate proved to be merely silver ortho-phosphate.[1] The filtrate from the silver salts gives an abundant pre-

[1] The reaction described above affords a convenient method for separating, at least approximately, ortho- from pyro-phosphoric acid. A solution of the acids—or their soluble salts—is acidified in the cold with nitric acid, and silver nitrate added in excess. On adding dilute ammonia, drop by drop, all the pyro-phosphoric acid is precipitated before any of the ortho-phosphoric acid comes down. At this point a single drop of ammonia gives a yellow tinge to the precipitate, which a drop of dilute nitric acid causes to disappear. If the liquid be now filtered, all the pyro-phosphoric acid will be in the precipitate and all the ortho-phosphoric acid in the filtrate. The reaction is so sharp that it might possibly be used to separate the acids quantitatively.

cipitate of silicic acid, when warmed with ammonia. The magnesia precipitate also shows the characteristic reaction of magnesium pyro-phosphate, dissolving in acetic acid when precipitated in the cold, and being reprecipitated from this solution on boiling.

The substance is therefore a derivative of pyro-phosphoric acid, and the formation of some ortho-phosphoric acid may be explained by the decomposition of the former—pyro-phosphoryl chloride dissolving in water with formation of ortho-phosphoric acid.[1]

Heated with phosphorus pentachloride at 100°, silico-pyro-phosphoryl chloride is readily and quantitatively converted into silicon tetrachloride and phosphorus oxychloride:

$$SiP_2O_6Cl_8 + 4PCl_5 = SiCl_4 + 6POCl_3.$$

The tetrachloride was isolated and expectations with regard to its nature were confirmed on converting it into the ether (b. p., 165.5°). No silicon oxychloride could be obtained. If heated with an insufficient amount of phosphorus pentachloride, the excess remains apparently unchanged.

The conversion of a derivative of silicic acid into silicon tetrachloride at so low a temperature has not been hitherto observed. R. Weber[2] obtained the tetrachloride and phosphorus oxychloride by passing the vapor of phosphorus pentachloride over silica at a red heat. As the pentachloride is completely dissociated at 300° into trichloride and chlorine, the reaction is due to the action of chlorine, combined with the reducing action of the trichloride—

$$SiO_2 + 2PCl_3 + 2Cl_2 = SiCl_4 + 2POCl_3—$$

which is analogous to the old method of preparing the tetrachloride—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

As I have convinced myself, phosphorus pentachloride does not act on amorphous silica (dried at 100°) even at 250°, further than to dehydrate it.

The action of a smaller quantity of phosphorus oxychloride on the trichlorhydrine is similar. 3 mol. trichlorhydrine and 1 mol. oxychloride, heated at 180°, gave ethyl chloride, silicon tetrachloride, and a solid product completely soluble in alcohol and water, the composition of which differed, however, from that of the substance above described. (Found: Si, 15.25; P, 22.30; Cl, 14.13.)

[1] Michaelis: Ber. d. chem. Ges. **4**, 767. [2] Ann. der Phys. Pogg. **112**, 619.

The action of an excess of phosphorus oxychloride on the chlorhydrines $SiCl_2(OC_2H_5)_2$ and $SiCl(OC_2H_5)_3$ is essentially similar. At 180°–200° a solid substance is formed, with much ethyl chloride and silicon tetrachloride. The amount of the tetrachloride is directly, and that of the solid inversely proportional to the amount of chlorine in the chlorhydrine. In each case the tetrachloride was isolated in a state of approximate purity, and converted into the ortho-ether, boiling at 165.5°. No other volatile substances could be detected. The solid body was completely soluble in alcohol, and, in brief, showed all the properties above described as belonging to silico-pyro-phosphoryl chloride.

The analysis of the product from $SiCl_2(OC_2H_5)_2$ gave—

	Calculated for $SiP_2O_6Cl_2$.	Found. I.	II.
Si	10.92	11.68	11.80
P	24.15	24.53	24.91

The product from $SiCl(OC_2H_5)_3$ gave—

	Calculated for $SiP_2O_6Cl_2$.	Found.
Si	10.92	10.15
P	24.15	24.54
Cl	27.59	24.73

The results, as before, are only approximate; but, it must be remembered, the body loses phosphorus oxychloride slowly on heating, and only the crude product could be analysed.

The reactions in these cases are—

$$4SiCl_2(OC_2H_5)_2 + 4POCl_3 = 2SiCl_4 + 2SiP_2O_6Cl_2 + 8C_2H_5Cl,$$
$$4SiCl(OC_2H_5)_3 + 6POCl_3 = SiCl_4 + 3SiP_2O_6Cl_2 + 12C_2H_5Cl.$$

Orthosilicic ether, $Si(OC_2H_5)_4$, was heated with excess of phosphorus oxychloride for two hours at 180°–200°. The tubes contained a solid substance and ethyl chloride. On distilling off the excess of oxychloride and decomposing it with water, only a trace of silica was left after evaporation, showing that practically no volatile silicon compound was formed. The solid, the properties of which were in every respect identical with those of the body above described, gave on analysis—

	Calculated for $SiP_2O_6Cl_2$.	Found. I.	II.	III.
Si	10.92	9.92	10.05	10.21
P	24.15	25.52	25.63	25.84
Cl	27.59	29.66	29.90	...

The reaction is, therefore, represented by the equation—

$$Si(OC_2H_5)_4 + 2POCl_3 = SiP_2O_6Cl_8 + 4C_2H_5Cl.$$

The constitution of the silico-phosphoryl chloride is possibly very complex. The simplest constitutional formula, deduced from the last equation, would be $Si\begin{cases} O > POCl \\ O \\ O \\ O > POCl \end{cases}$; but as this would give no pyro-phosphoric acid on decomposition with water, we must assume that it is $SiO < \begin{matrix} O.PO.Cl \\ O.PO.Cl \end{matrix} > O$; or a polymer containing the group —O.PO.O.PO.O—, which makes it a derivative of metasilicic acid. The cause of the formation of silicon tetrachloride from the chlorhydrines is not clear. It is obviously not due to a direct replacement of ethoxyl by chlorine, for then it should be obtained in the same amount from each chlorhydrine, or from the ether; whereas the latter does not give it, and the amount obtained from the former is proportional to the amount of chlorine they already contain. Besides, no phosphoric ethers are formed. Nor does the supposition explain the formation of silico-pyrophosphoryl chloride in quantities inversely as the amount of chlorine. A possible explanation is the following: The chlorhydrines[1] are formed by heating mixtures of orthosilicic ether with silicon tetrachloride, or of either of these with other chlorhydrines, that one being formed in largest amount which corresponds in composition to the mean composition of the mixture; for example—

$$3Si(OC_2H_5)_4 + SiCl_4 = 4SiCl(OC_2H_5)_3.$$
$$2SiCl_3(OC_2H_5) + Si(OC_2H_5)_4 = 3SiCl_3(OC_2H_5)_2.$$

These reactions take place below 200°: partial dissociation occurring, the products reuniting to form that body which tends to give the liquid a homogeneous composition. Doubtless the reverse process takes place at the same time; for example—

$$4SiCl(OC_2H_5)_3 = 3Si(OC_2H_5)_4 + SiCl_4;$$

and if phosphorus oxychloride be present—which, as just shown, destroys the ether—this can go on until all the chlorhydrine has been converted into ether and tetrachloride. This explanation is

[1] Friedel and Crafts: Ann. chim. phys. [4] 9, 11, 14, 15.

simple enough, but, as shown by the action of phosphorus oxychloride on *disilicic* chlorhydrines, the actual process is possibly more complicated.

By heating a mixture of trichlorhydrine, phosphorus and iodine, a solid of similar properties was obtained, and silicon tetrachloride was formed. The reaction was not followed further.

Action of Phosphorus Oxychloride on Derivatives of Disilicic Acid.

Hexethyl disilicate,[1] $O<\frac{Si(OC_2H_5)_3}{Si(OC_2H_5)_3}$, was heated with an excess of phosphorus oxychloride in sealed tubes at 180°–200° for two or three hours. The tubes contained a white solid, outwardly resembling silico-pyrophosphoryl chloride, and much ethyl chloride. No volatile silicon compound was formed. The solid resembled in its general properties the one described. It was completely soluble in alcohol, and therefore contained no free silica. The solution gave the reactions of pyro-phosphoric acid. It differed markedly in composition from the ortho-silicic derivative, the analysis giving—

	Calculated for $SiP_2O_6Cl_2$.	Found.
Si	10.92	17.03
P	24.15	23.91
Cl	27.59	21.04

This corresponds to no probable formula, but contains 4 atoms Si to 5 atoms P, instead of 1 atom Si to 2 atoms P. Phosphorus pentachloride converts it readily (at 100°) into silicon tetrachloride and phosphorus oxychloride. No silicon oxychloride is formed, the product passing over entirely below 112°. The tetrachloride was isolated and converted into the tetrethyl ether (boiling at 165.5°).

The ease with which the ortho-chlorhydrines give, with phosphorus oxychloride, silicon tetrachloride, led to an analogous experiment with the *disilicic chlorhydrines*, in the hope that in this way silicon oxychloride might be obtained. On the above hypothesis, we should have, in the presence of phosphorus oxychloride, the following reaction:

$$6O<\frac{SiCl_3}{SiCl_2(OC_2H_5)} = 5O<\frac{SiCl_3}{SiCl_3} + O<\frac{Si(OC_2H_5)_3}{Si(OC_2H_5)_2};$$

and analogous reactions with the other chlorhydrines.

[1] Friedel and Crafts: Ann. chim. phys. [4] 9, 24.

The disilicic chlorhydrines, which have not hitherto been prepared, are formed by heating disilicic ether with an excess of silicon tetrachloride for several hours at 200°. A gradual exchange of ethoxyl and chlorine occurs, disilicic chlorhydrines and orthosilicic trichlorhydrine being formed. After distilling off the latter, the residue is again heated with silicon tetrachloride, whereby the conversion is carried further. In this way a mixture of disilicic chlorhydrines was obtained, which, after freeing from all orthosilicic compounds by repeated distillation, boiled at 170°–220°. A chlorine determination showed that it contained the equivalent of 65 per cent. Si_2OCl_6. No attempt was made to isolate any of these chlorhydrines, as no less than eight are theoretically possible, and it was presumed that they would all act in the same way toward phosphorus oxychloride. The mixture was heated with excess of phosphorus oxychloride (based on the amount of chlorine shown by analysis) for two and a half hours at 180°–200°; after which no further action was observed. The appearance of the product was the same as in previous experiments. The liquid product was distilled off and fractioned. It was found to consist of an excess of phosphorus oxychloride, of *silicon tetrachloride*, which was recognised through conversion into the ether, and ethyl-chloride. The liquid boiled entirely below 112°, and therefore none of the expected silicon oxychloride was formed. The solid product was markedly different from those before obtained. It was only partly soluble in alcohol, and on boiling out with the solvent, a large residue of *silica* was left. Besides a soluble silico-phosphoryl chloride and ethyl chloride, the only products were silicon tetrachloride and silica. If the oxychloride be formed at all, it is at once decomposed in the presence of phosphorus oxychloride—

$$2Si_2OCl_6 = 3SiCl_4 + SiO_2.$$

Whether this actually occurs is questionable, as the oxychloride and all the other substances concerned are, by themselves, stable at a much higher temperature than that employed. I am unable to give any satisfactory explanation of the reaction.

Amorphous silica, prepared from water-glass and dried at 100°, gives with phosphorus oxychloride a small amount of silico-phosphoryl chloride, soluble in alcohol: 3.5 per cent. of the silica was converted into this compound.

The silicon tetrachloride used as the starting-material of these experiments was made by the admirable method of Gattermann.[1] For preparing the silicon mixture I used, instead of test-tubes, sheet-iron crucibles of about 200 cc. capacity. These are nearly filled with an intimate mixture of three parts quartz powder and one part magnesium powder, tightly pressed down. On heating over a blast-lamp, the reaction starts in a few seconds, and is indicated by the whole crucible suddenly becoming red-hot. During the reaction the lid must be held down firmly. I prefer to extract the magnesia from this product before using it, as less care has to be used in regard to temperature when passing chlorine over it. By using ice alone, to condense the chloride, nearly the theoretical yield is obtained: the crude product loses about 15 per cent. in the process of purification.

The *orthochlorhydrines* were prepared essentially according to the method of Friedel and Crafts (*l. c.*). Any mixture may be used which coincides in composition with that of the chlorhydrine desired. The yield is never theoretical, no matter how long the heating may be continued. The yields of pure substance, obtained after six distillations, were as follows: Monochlorhydrine, 65 per cent.; dichlorhydrine, 40 per cent.; trichlorhydrine, 47 per cent. More can, of course, be obtained by uniting and heating the residues.

Friedel and Crafts[2] obtained the disilicic ether by adding to silicon tetrachloride, drop by drop, alcohol containing the calculated amount of water. They claim that the yield is nearly theoretical. I am not able to confirm this statement. By following their directions exactly, I obtained a mixture of ortho and disilicic ethers, with ethers of much higher boiling-points. After repeated fractioning, only 33 per cent. of the theoretical yield of disilicic ether was obtained, and the amount of ortho-ether was much greater. This is due to the fact that the added water acts on the disilicic ether already formed, giving more complex bodies, so that there is an excess of tetrachloride, which is converted into ortho-ether.

The essential results of these experiments may be summed up as follows:

Phosphorus oxychloride acts on orthosilicic ether and its chlorine derivatives according to the following equations:

[1] Ber. d. chem. Ges. **23**, 186-8. [2] Ann. chim. phys. [4] **9**, 26.

I. $4Si(OC_3H_5)_4 + 8POCl_3 = 4SiP_3O_6Cl_3 + 16C_3H_5Cl.$

II. $4SiCl(OC_3H_5)_3 + 6POCl_3 = SiCl_4 + 3SiP_2O_6Cl_2 + 12C_3H_5Cl.$

III. $4SiCl_3(OC_3H_5)_2 + 4POCl_3 = 2SiCl_4 + 2SiP_3O_6Cl_3 + 8C_3H_5Cl.$

IV. $4SiCl_3(OC_3H_5) + 2POCl_3 = 3SiCl_4 + SiP_3O_6Cl_3 + 4C_3H_5Cl.$

The body $SiP_2O_6Cl_2$ is the chloride of a silico-pyrophosphoric acid, is decomposed by water into silica and pyrophosphoric acid, and is easily converted by phosphorus pentachloride into silicon tetrachloride and phosphorus oxychloride.

The ether of disilicic acid acts similarly, giving a silico-phosphoryl chloride of different composition but analogous properties.

The chlorhydrines of disilicic acid do not give with phosphorus oxychloride, as might be inferred, a silico-phosphoryl chloride and silicon oxychloride, but a mixture of the first with free silica and silicon tetrachloride.

Phosphorus trichloride also acts on orthosilicic ether at 200°, giving a white solid, and liquid products, which will be further studied.

In conclusion, I wish to express my indebtedness to Prof. F. W. Clarke for liberally placing at my disposal the means of carrying out these experiments.

U. S. Geological Survey, Washington, *February*, 1891.

ON THE ATOMIC WEIGHT OF OXYGEN.

By E. H. Keiser.

In a recent paper[1] on this subject, Mr. W. A. Noyes makes a statement which is not in accordance with the facts, and which, as it may be misleading to some, deserves to be corrected. Mr. Noyes states that he has pointed out a source of error in my determinations of the atomic weight of oxygen. I desire to call attention to the fact that Mr. Noyes has merely pointed out what he *supposes* to be a source of error in my determinations, which is quite different from having pointed out a source of error. Moreover, Mr. Noyes's supposition is not well founded, and is not in accordance with the results of experiments.

[1] Journal of Analytical and Applied Chemistry **5**, 36; Ber. d. chem. Ges. **24**, 238.

The point in question is this: It was found as the result of direct experiments that the hydrogen which was driven out of the palladium tube contained a trace of moisture; this moisture was collected in a phosphorus-pentoxide tube, and its weight was subtracted from the apparent weight of hydrogen. Mr. Noyes thinks that there could not have been moisture present in the hydrogen, and that the increase in weight of the pentoxide tube should not have been deducted from the apparent weight of hydrogen. But I had found by direct experiment that moisture was present, and was, therefore, obliged to insert a weighed phosphorus-pentoxide tube. Mr. Noyes thinks that the moisture came from the gases that were subsequently passed through the tube, but, as I have clearly stated in my paper, these gases were thoroughly dried by passing through concentrated sulphuric acid and over phosphorus pentoxide before entering the tube in question, so that this supposition is also without foundation.

The fact remains that the atomic weight of oxygen as determined by the combustion of weighed amounts of hydrogen, the hydrogen being obtained from palladium hydrogen, is 15.95, and not a lower value, as Mr. Noyes thinks he has shown it to be. Nor can I agree with his statement that it is almost certain that the true atomic weight of oxygen is not greater than 15.90. Before coming to such a conclusion, it is well to remember that all recent determinations of this atomic weight, like the older ones of Dumas, and Erdmann and Marchand, have been determinations of the composition of water *by difference*, that is, only two of the three quantities have been determined directly. In all the determinations it is assumed that the hydrogen or oxygen which is weighed is really all present in the weighed quantity of water, or, that the hydrogen and oxygen which have been weighed have combined completely with one another. In other words, no *complete syntheses* of water have yet been recorded. The words *complete syntheses* are here used in the sense in which they were used by Stas in his researches on the atomic weights of silver, chlorine, etc. To make a complete synthesis of water it is necessary to weigh separately the hydrogen, the oxygen, and the water formed by the union of the weighed amounts of hydrogen and oxygen. It seems to me that it is too early to come to any conclusion as to the true value of the relation between hydrogen and oxygen until this relation shall have been determined by the complete gravimetric synthesis of water.

I have recently made determinations of the atomic weight of oxygen by a method which permits of the separate weighing of the hydrogen, the oxygen and the water. In brief the method is as follows: A glass vessel containing spongy palladium and provided with a three-way stop-cock is exhausted with an air-pump, and as perfect a vacuum obtained as is possible with a mercury-pump, and the weight of the empty vessel determined. Pure hydrogen from hot palladium is passed over phosphorus pentoxide and into the exhausted vessel. After the spongy palladium is saturated with the gas, the vessel is again exhausted, and the increase in weight after again weighing is the weight of hydrogen occluded. Pure oxygen is now admitted to the palladium hydrogen until present in excess; the hydrogen is completely converted into water at low temperatures. The weight of oxygen admitted is determined by again weighing the vessel. Now a weighed phosphorus-pentoxide U-tube is attached to the palladium vessel, and the excess of oxygen, together with any nitrogen if it was present in the oxygen, is removed by the air-pump. The loss in weight of the palladium vessel and the pentoxide tube (both weighed together) gives the excess of oxygen. The water is thereupon completely transferred from the palladium to the pentoxide tube, and the increase in weight of the latter gives the weight of water formed. The weights of the hydrogen, oxygen and water are thus determined separately and by direct weighings. Two weighings are involved in the determination of the hydrogen, two weighings also give the weight of water, and from three weighings the weight of oxygen is obtained. Thus far I have made three determinations, and in each one the sum of the weights of hydrogen and oxygen agrees with the weight of water found to within .2 of a milligram, and the weight of the palladium tube at the end of the determination was found to be the same as at the beginning. The three results agree quite closely with one another, and give for the atomic weight of oxygen almost exactly the whole number, 16. After a larger number of determinations have been made I shall publish the details of the method and of each separate determination.

I shall not here enter into a critical discussion of the method used by Mr. Noyes. It might lead to a controversy and a waste of time. It would, however, not be difficult for any thoughtful reader of his paper to see where inaccuracies might perhaps

have crept into the work, and several sources of error have already been shown by Mr. G. S. Johnson[1] to exist in the method, which, it seems to me, have not been completely disproved by Mr. Noyes. Nor is it possible to regard the use of sticks of caustic potash for the purification of hydrogen as unobjectionable. The sticks, as Mr. Noyes states, gradually dissolved in the water carried over. But sticks of potash contain air, and when they dissolve the air is set free, and thus the hydrogen is rendered impure.

BRYN MAWR, PA., *March*, 1891.

ON ORTHO-SULPHO-PARA-TOLUIC ACID AND SOME OF ITS DERIVATIVES.

BY WYATT W. RANDALL.

Introduction.

Investigations upon the sulphonic acids derived from para-toluic acid by the replacement of a hydrogen atom of the benzene nucleus by the sulphoxyl group, $-SO_3H$, have up to this time been almost entirely confined to that one of the two isomeric substances represented by the formula $C_6H_3\begin{cases}CO.OH & (1)\\ SO_2.OH & (3)\\ CH_3 & (4)\end{cases}$; that is, meta-sulpho-para-toluic acid. Flesch,[2] Bechler,[3] Fischli,[4] Remsen and Burney,[5] R. Meyer and Baur,[6] and Remsen and Emerson[7] prepared this acid and examined its derivatives. On the other hand, the only work on record upon the isomeric acid, $C_6H_3\begin{cases}CO.OH & (1)\\ SO_2.OH & (2)\\ CH_3 & (4)\end{cases}$, is that of Fittica,[8] who claims to have prepared the substance from thio-thymol, $C_6H_3\begin{cases}CH_3 & (1)\\ SH & (3)\\ C_3H_7 & (4)\end{cases}$, by oxida-

[1] Chem. News **59**, 272.
[2] J. prakt. Chem. [2] **8**, 167.
[3] This Journal **2**, 405.
[4] This Journal **8**, 264.
[5] Ber. d. chem. Ges. **6**, 478.
[6] Ber. d. chem. Ges. **12**, 616.
[7] Ann. Chem. (Liebig) **220**, 18.
[8] Ann. Chem. (Liebig) **172**, 327.

tion by means of nitric acid, and this thio-thymol in turn was obtained by the action of phosphorus pentasulphide upon thymol, $C_6H_3\begin{cases}CH_3\\OH\\C_3H_7\end{cases}$. Fittica distinguishes between this ortho-sulpho-para-toluic acid and its isomer by the following characteristics which he claims to have established, *viz.* (1) that the acid crystallises from a solution in alcohol without water of crystallisation, (2) that the acid is insoluble in water,[1] and (3) that it forms a magnesium salt which when crystallised from absolute alcohol contains no water of crystallisation. Further, he says that he was unable to prepare salts of the acid with potassium, sodium or barium, since with solutions of the hydroxides of these metals the crystallised acid blackened, and the solution after filtration contained the sulphur of the sulpho-acid in the form of sulphate. He gives 190° as the melting-point of the acid.

"*Methyl-saccharin.*"

The investigations of Fittica upon ortho-sulpho-para-toluic acid and its derivatives were much hindered by reason of the difficulty of obtaining any of these compounds in pure form and in any quantity. Recently, however, a new sulphinide has been prepared which can be transformed with no great difficulty into ortho-sulpho-para-toluic acid, and which can be procured in sufficient quantity to render a thorough investigation of this field possible. This sulphinide is "methyl-saccharin," or, more properly, para-toluic sulphinide, of the formula $C_6H_3\begin{cases}CO\\SO_2\\CH_3\end{cases}>NH\ \begin{matrix}(1)\\(2).\\(4)\end{matrix}$

The method, use of which is made for its preparation, was devised by the "Badische Anilin- und Soda-fabrik,"[2] and is as follows: Para-toluidine is transformed into para-toluidine-meta-sulphonic acid[3]; by means of the Sandmeyer reaction[4] the amido group is replaced by cyanogen, forming para-cyan-toluene-meta-sulphonic acid. By the action of phosphorus pentachloride is formed the chloride of this acid, and from this the amide is prepared. This is then transformed into ortho-sulphonamine-para-toluic acid, and, finally, this acid, on being heated above its melting-point, passes

[1] See also Meyer and Baur, Ann. Chem. (Liebig) **220**, 22.
[2] Ber. d. chem. Ges. **22**, Referate, 719.
[3] Nevile and Winther, Ibid. **13**, 1947.
[4] Ibid. **17**, 2650.

into para-toluic sulphinide. The successive products of these several reactions are represented by the following formulæ:

$$C_6H_4\begin{cases}NH_2\ (1)\\CH_3\ (4)\end{cases} \rightarrow C_6H_3\begin{cases}NH_2 \quad (1)\\SO_2.OH\ (2)\\CH_3 \quad (4)\end{cases} \rightarrow C_6H_3\begin{cases}CN\\SO_2.OH \rightarrow\\CH_3\end{cases}$$

$$C_6H_3\begin{cases}CN\\SO_2.Cl \rightarrow\\CH_3\end{cases} C_6H_3\begin{cases}CN\\SO_2.NH_2 \rightarrow\\CH_3\end{cases} \quad C_6H_3\begin{cases}CO.OH\\SO_2.NH_2 \rightarrow\\CH_3\end{cases}$$

$$C_6H_3\begin{cases}CO\\SO_2\end{cases}>NH\ \begin{matrix}(1)\\(2).\\(4)\end{matrix}$$

The Badische Anilin- und Sodafabrik most courteously placed at the disposal of Prof. Remsen the para-toluic sulphinide or "methyl-saccharin" which served as the starting-point in the present investigation, and at his suggestion I undertook the work, an account of which is given below.[1]

I may as well say at this point that in speaking of this substance as the "ortho-sulpho-," rather than the "meta-sulpho-," para-toluic acid, I have followed the nomenclature adopted by Beilstein in his "Handbuch der Organischen Chemie," and have prefixed such terms as will indicate the positions of the other groups with reference to the carboxyl group taken as the starting-point.

Ortho-sulpho-para-toluic Acid.

In order to obtain the free ortho-sulpho-para-toluic acid from para-toluic sulphinide, advantage was taken of the transformation brought about by boiling sulphinides with dilute hydrochloric acid. This reaction, studied by Remsen and Burton,[2] who experimented upon the transformation by its means of benzoic sulphinide into acid ammonium ortho-sulpho-benzoate,—

$$C_6H_4<\begin{matrix}SO_2\\CO\end{matrix}>NH + 2H_2O = C_6H_4<\begin{matrix}SO_2.ONH_4\\CO.OH\end{matrix},$$

was equally applicable for the corresponding transformation of para-toluic sulphinide. The operation was conducted with portions of the sulphinide of 25 grams each, in flasks fitted with reflux-

[1] I take this opportunity of expressing my thanks to the Company for their liberality.—I. R.
[2] This Journal **11**, 403-405.

condensers. In each flask was poured 600 cc. dilute hydrochloric acid, prepared by mixing 100 cc. pure concentrated acid with 500 cc. water. After the boiling had been continued a half-hour, all the sulphinide had passed into solution. At the end of 45 or 50 minutes the heating was discontinued, and it was found that on cooling no sulphinide crystallised out. Moreover, the sweet taste had disappeared from the solution. The latter was then evaporated to dryness, to be rid of hydrochloric acid, redissolved and evaporated to crystallisation.

The transformation was precisely similar to that of benzoic sulphinide, the product in the case of para-toluic sulphinide being the acid ammonium salt of ortho-sulpho-para-toluic acid, the reaction by which it is produced being represented as follows:

$$C_6H_3\begin{cases} CO \\ SO_2 \\ CH_3 \end{cases}\!\!>NH + 2H_2O = C_6H_3\begin{cases} CO.OH & (1) \\ SO.ONH_4 & (2). \\ CH_3 & (4) \end{cases}$$

The transformation of the acid ammonium salt into the acid chloride was brought about by mixing the dry, finely-powdered salt with about twice its weight of phosphorus pentachloride in a small Erlenmeyer flask, and shaking the two together. The reaction began immediately. After the evolution of acid fumes had to a great extent ceased, the flask was placed in a bath of sulphuric acid, and heated for some time at about 120° in order to be rid of phosphorus oxychloride. Unless this precaution be taken, there is likely to be loss in the subsequent washing with water, since the heat generated by the reaction of phosphorus oxychloride and water, will convert a large part of the acid chloride, in the presence of water, into the free acid, which is easily soluble. After the substance had been allowed to cool, the chloride was washed with cold water several times, and was then placed with a considerable amount of pure water in a flask connected with a reflux-condenser, and boiled until the oil had entirely disappeared. As this solution of the free acid was colored slightly yellow under these conditions, a little animal-charcoal was added and the boiling continued a short time. The solution, on being filtered and evaporated to dryness, to be rid of the hydrochloric acid formed in the reaction, redissolved, and again evaporated, yielded the crystallised ortho-sulpho-para-toluic acid.

The transformation of the acid ammonium salt into the free acid would be represented by the following equations:

(1). $C_6H_3\begin{cases}CO.OH\\SO_2.ONH_4\\CH_3\end{cases}+2PCl_5=$

and $C_6H_3\begin{cases}CO.Cl\\SO_2.Cl\\CH_3\end{cases}+2POCl_3+NH_4Cl+HCl;$

(2). $C_6H_3\begin{cases}CO.Cl\\SO_2.Cl\\CH_3\end{cases}+2H_2O=C_6H_3\begin{cases}CO.OH\\SO_2.OH\\CH_3\end{cases}+2HCl.$

Thus obtained, ortho-sulpho-para-toluic acid crystallises from concentrated aqueous solution in what appear to be tetragonal prisms terminated by planes belonging to the pyramid of the second order. The composition of the crystallised acid is represented by the formula $C_6H_3\begin{cases}CO.OH\\SO_2.OH\\CH_3\end{cases}+3\frac{1}{2}H_2O$, as is indicated by the analyses given below:

I. 0.1824 gram hydrous acid gave 0.2292 gram CO_2 and 0.0866 gram H_2O.

II. 0.3029 gram hydrous acid gave 0.3874 gram CO_2 and 0.1532 gram H_2O.

III. 0.2620 gram hydrous acid gave 0.2212 gram $BaSO_4$.

IV. 0.41165 gram hydrous acid gave 0.3520 gram $BaSO_4$.

Calculated for $C_6H_3\begin{cases}CO.OH\\SO_2.OH\\CH_3\end{cases}$;	$C_6H_3\begin{cases}CO.OH\\SO_2.OH\\CH_3\end{cases}+3H_2O$;	$C_6H_3\begin{cases}CO.OH\\SO_2.OH\\CH_3\end{cases}+4H_2O$.
C 44.44	35.55	33.33
H 3.74	5.185	5.55
S 14.85	11.85	11.11

Calculated for $C_6H_3\begin{cases}CO.OH\\SO_2.OH\\CH_3\end{cases}+3\frac{1}{2}H_2O$.	Found. I.	II.	III.	IV.
C 34.41	34.28	34.88	...	...
H 5.38	5.275	5.62	...	...
S 11.47	...	...	11.59	11.74

Several attempts were made to determine exactly the water of crystallisation by heating the crystallised acid. The acid becomes anhydrous when heated for a long time at from 135°–140°. In each case, after the water had been driven off in amount closely approximating $3\frac{1}{2}$ molecules, the anhydrous acid began to volatilise, as was evident from the white fumes evolved. The exact conditions necessary for dehydrating the acid without bringing

about volatilisation, were not found. The anhydrous acid melts at 158°.

Ortho-sulpho-para-toluic acid is dibasic, forming two sets of salts with metals. It is soluble in alcohol and in ether. It is also, in spite of the statement of Fittica to the contrary, very easily soluble in water. Its aqueous solution has to be quite concentrated before it will show signs of crystallisation. The solution, indeed, can be evaporated, without crystals separating out, to such a point that, when allowed to cool, the whole contents of the dish will become solid.

The crystals of the acid appear to be tetragonal, but on account of the rounding of the angles and the etching of the prismatic faces, due to its great solubility in water, a careful crystallographic study of the acid would have been impossible. The acid under some conditions is slightly efflorescent in the air, the clear-white crystals becoming opaque.

Chloride of Ortho-sulpho-para-toluic Acid.

In describing the preparation of ortho-sulpho-para-toluic acid, it was stated that the chloride of the acid is formed by the action of phosphorus pentachloride upon the acid ammonium salt of the acid, as indicated in the equation:

$$C_6H_3\begin{cases}CO.OH\\SO_2.ONH_4\\CH_3\end{cases} + 2PCl_5 =$$

$$C_6H_3\begin{cases}CO.Cl\\SO_2.Cl\\CH_3\end{cases} + NH_4Cl + HCl + 2POCl_3.$$

The chloride thus prepared is an oil whose melting-point is 59°. It is therefore solid at ordinary temperatures. It is purified by recrystallisation from "petroleum ether," and is thus obtained in crystals which are probably triclinic. It is easily soluble in ether and less readily in alcohol. Boiled with water it is transformed into the free acid and hydrochloric acid, according to the equation:

$$C_6H_3\begin{cases}CO.Cl\\SO_2.Cl\\CH_3\end{cases} + 2H_2O = C_6H_3\begin{cases}CO.OH\\SO_2.OH\\CH_3\end{cases} + 2HCl.$$

For the purpose of analysis 0.1720 gram of the acid chloride was heated with pure water in a sealed tube until the oil had entirely disappeared. The tube, when it had become cold, was

opened, the contents washed into a beaker, and the total amount of free acid present determined by means of a standard solution of ammonia. Since for each molecule of chloride decomposed one molecule of the dibasic acid and two molecules of hydrochloric acid are formed, one half of the ammonia added must have been employed in neutralising the hydrochloric acid. The quantity of the latter acid, and consequently the proportion of chlorine in the original chloride, may thus be readily deduced. Total quantity of ammonia solution required for neutralisation = 26.00 cc., which is equivalent to 0.0463 gram NH_3.

Calculated for $C_6H_3\begin{cases}CO.Cl\\SO_2.Cl.\\CH_3\end{cases}$	Found.
28.37	28.04

Salts of Ortho-sulpho-para-toluic Acid.

Salts of ortho-sulpho-para-toluic acid were prepared as follows: The neutral salts of potassium, ammonium, barium, calcium, magnesium, and silver; and the acid salts of potassium, ammonium, barium, calcium, and magnesium. The statement of Fittica[1] that the hydroxides of the alkali metals decompose the acid with the formation of sulphates, I have been unable to verify. The free acid, boiled with strong solutions of potassium, sodium and barium hydroxides, passes into solution without carbonisation or other signs of disintegration. The salts are stable. The silver salt does not give up its "water of crystallisation" until a temperature of 215° is reached, while the neutral calcium salt requires that the temperature be raised to 260° before it will become anhydrous. Even the *acid barium salt* is not rendered anhydrous until the temperature reaches 235°. The neutral potassium salt is not very rapidly decomposed by fused caustic potash. These facts certainly seem to show that it was not ortho-sulpho-para-toluic acid with which Fittica obtained these results.

The acid salts, as would be expected, are readily converted by boiling with metallic hydroxides or carbonates into neutral salts. No mixed salt of this acid was prepared, however, although compounds analogous to the silver-ammonium ortho-sulpho-benzoate, $C_6H_4\begin{cases}CO.OAg\\SO_2.ONH_4\end{cases}$, prepared by Dohme and described in his dissertation, could in all probability readily be made.

[1] Ann. Chem. (Liebig) **172**, 328-9.

Although it has not been proved, it will be assumed that in the acid salts the metal replaces the hydrogen of the sulphoxyl, rather than the carboxyl group, the general formula of these salts being, therefore, $C_6H_3\begin{cases}CO.OH\\SO_2.OM\\CH_3\end{cases}$, where M represents an atom of any univalent metal. The acid salts are as a rule less soluble than the neutral. All the salts prepared were clear and colorless, the silver salt, of course, turning dark if exposed to the light. On account of their extreme solubility in water, crystals of both acid and neutral salts were as a rule without well-defined edges. No attempts at crystallographic measurement were made.

Neutral Salts of Ortho-sulpho-para-toluic Acid.

Neutral Potassium Salt, $C_6H_3\begin{cases}CO.OK\\SO_2.OK\\CH_3\end{cases} + xH_2O$.—This salt was prepared by simply neutralising a solution of the free acid by means of potassium carbonate solution. It is, like all the other neutral salts of ortho-sulpho-para-toluic acid with the exception of the silver salt, extremely soluble in water. A solution evaporated to the consistency of a syrup and placed over sulphuric acid in a desiccator, refused to crystallise, and after a month's time finally dried to a white, semi-crystalline crust. No analysis of the salt was made, but by fusion with caustic potash the sulphonic acid residue was replaced by the hydroxyl group, and ortho-hydroxy-para-toluic acid was formed. This reaction will be taken up for discussion later on.

Neutral Ammonium Salt, $C_6H_3\begin{cases}CO.ONH_4\\SO_2.ONH_4\\CH_3\end{cases} + 2\frac{1}{2}H_2O$.—This salt is formed by boiling the solution of the acid ammonium salt with an excess of solution of ammonia. The boiling is continued until all excess of ammonia is removed. The salt is exceedingly soluble in water; the solution placed over sulphuric acid in a desiccator becoming concentrated to a syrupy condition before crystallisation begins, the salt being finally deposited as a crust on the bottom of the vessel containing it. Two analyses of the salt were made, the method being to decompose by means of caustic soda solution in a Kjeldahl apparatus. The ammonia given off was absorbed in a standard solution of hydrochloric

acid and the quantity determined by titration. The results obtained are expressed by the following figures:

I. 0.1942 gram of the salt gave 0.02237 gram NH_3.

II. 0.2549 gram of the salt gave 0.02954 gram NH_3.

	Calculated for $C_6H_3\{CO.ONH_4, SO_2.ONH_4, CH_3 + 2\frac{1}{2}H_2O$.	Found. I.	II.
N	9.49	9.49	9.54

Neutral Barium Salt, $C_6H_3\{\begin{matrix}CO.O\\SO_2.O\end{matrix}>Ba, CH_3$.—This salt was made by boiling a solution of ortho-sulpho-para-toluic acid with an excess of pure barium carbonate; and also by boiling a solution of the acid ammonium salt with an excess of the same reagent until no more ammonia was given off; filtering and evaporating to crystallisation. The salt forms fine, white needles which contain no water of crystallisation. The following results were obtained on analysing the salt:

I. The dry salt heated at 190° did not lose appreciably in weight.

II. 0.2706 gram of the salt yielded 0.1784 gram $BaSO_4$.

III. 0.39515 gram of the salt yielded 0.2611 gram $BaSO_4$.

	Calculated for $C_6H_3\{\begin{matrix}CO.O\\SO_2.O\end{matrix}>Ba, CH_3$.	Found. I.	II.
Ba	39.03	38.77	38.85

Neutral Calcium Salt, $C_6H_3\{\begin{matrix}CO.O\\SO_2.O\end{matrix}>Ca, CH_3 + H_2O$.—The method of preparation of this salt was merely to boil a solution of the free acid with an excess of calcium carbonate in the form of powdered Iceland spar. After evaporating the filtered solution to a small volume and allowing it to stand several weeks over sulphuric acid in a desiccator, the salt crystallised in clear, colorless prisms, apparently monoclinic, extended parallel to the clino-pinachoidal faces. The crystals contain one molecule of "water of crystallisation," and hold it with such tenacity that the salt is not rendered anhydrous until a temperature of 255°–260° is attained. The anhydrous salt is very hygroscopic. The following figures were obtained on analysis:

I. 0.2772 gram of the salt yielded 0.1381 gram $CaSO_4$.

II. 0.2105 gram of the salt yielded 0.1044 gram $CaSO_4$.

III. 0.2304 gram of the salt, heated at 260°, lost 0.0154 gram in weight.

	Calculated for $C_6H_3\{^{CO.O}_{SO_2.O}>Ca + H_2O$.	Found. I.	II.	III.
Ca	14.71	14.65	14.58	...
H_2O	6.61	...	...	6.63

Neutral Magnesium Salt, $C_6H_3\{^{CO.O}_{SO_2.O}>Mg + xH_2O$.— This salt is described by Fittica[1] as crystallising from absolute alcohol in yellow crystals without water of crystallisation, the color being probably due to impurity. The salt was prepared in the course of this investigation by boiling a solution of the free acid with magnesium carbonate, filtering and evaporating. Evaporated to dryness from aqueous solution, on the water-bath or in a desiccator, it hardens to a yellowish, gummy mass with no evidence of crystallisation. The same result was obtained from a solution in ordinary alcohol. The solution in absolute alcohol, however, on evaporation leaves a white, deliquescent paste—apparently a mass of fine, white crystals. I did not have time at my disposal to prepare this salt in proper condition for analysis.

Neutral Silver Salt, $C_6H_3\{^{CO.OAg}_{SO_2.OAg} + 1\frac{1}{2}H_2O$.— This salt is formed by boiling a solution of ortho-sulpho-para-toluic acid with an excess of silver oxide. The filtered solution, if not too concentrated, on cooling deposits the salt in the form of beautiful, strongly-refracting, colorless rhombohedra. If the solution be at all concentrated—and the salt is only slightly soluble even in boiling water,—instead of crystals, a yellow amorphous precipitate is obtained. The crystals are very slightly, if at all, soluble in cold water. They contain $1\frac{1}{2}$ molecules of "water of crystallisation." As would be expected, exposure to daylight renders the crystals dark-brown in color and opaque. In analysing this salt, the silver was determined as chloride, by precipitating by means of hydrochloric acid from a hot aqueous solution; and also as sulphate, by decomposing the compound by heating with strong sulphuric acid. These analyses gave the following results:

[1] Loc. cit.

I. 0.4747 gram of the salt gave 0.2972 gram AgCl.

II. 0.3175 gram of the salt gave 0.2167 gram Ag_2SO_4.

III. 0.3761 gram of the salt, heated at 215°, lost 0.0225 gram in weight.

	Calculated for $C_6H_3\begin{cases}CO.OAg\\SO_2.OAg\\CH_3\end{cases}+1\frac{1}{2}H_2O$.	Found. I.	II.	III.
Ag	47.26	47.15	47.25	...
H_2O	5.91	...	...	5.97

Acid Salts of Ortho-sulpho-para-toluic Acid.

Acid Potassium Salt, $C_6H_3\begin{cases}CO.OH\\SO_2.OK\\CH_3\end{cases}$.—The method employed for the preparation of this salt, as well as of the acid barium and acid calcium salts, was that usually employed in preparing the acid salts of bibasic acids, *viz.* the acid solution was divided into two equal parts, one of which was neutralised by means of a carbonate, and the other then added. This salt forms ortho-rhombic prisms, when crystallised from water, and contains no water of crystallisation. On analysis:

I. 0.5060 gram of the salt gave 0.1701 gram K_2SO_4.

II. 0.5530 gram of the salt gave 0.18595 gram K_2SO_4.

	Calculated for $C_6H_3\begin{cases}CO.OH\\SO_2.OK.\\CH_3\end{cases}$	Found. I.	II.
K	15.38	15.09	15.09

Acid Ammonium Salt, $C_6H_3\begin{cases}CO.OH\\SO_2.ONH_4\\CH_3\end{cases}$.—This salt is formed, as has before been stated, by the action of dilute hydrochloric acid upon para-toluic sulphinide. That the acid salt and *not* the free acid, is the product of this action, is certainly very interesting. The crystals of the salt are probably rhombohedral. Single crystals suitable for measurement are difficult to obtain, the tendency of the salt to form complicated crystal-aggregates being very marked. Treated with ammonia, the acid ammonium salt is converted into the neutral ammonium salt. Boiled with an excess of barium carbonate, ammonia is given off and the neutral barium salt formed. Phosphorus pentachloride converts this salt into the chloride of ortho-sulpho-para-toluic acid, as has been described. On analysis the following results were obtained:

I. 0.1812 gram of the salt gave 0.01307 gram NH_3.

II. 0.2272 gram of the salt gave 0.01607 gram NH_3.

	Calculated for $C_6H_3\begin{cases}CO.OH\\SO_2.ONH_4\\CH_3\end{cases}$.	Found. I.	II.
N	6.01	5.94	5.83

The ammonia was determined by decomposing a known weight of the salt in a Kjeldahl apparatus by means of caustic soda solution, and fixing the ammonia given off with the aid of a solution of standard hydrochloric acid.

Acid Barium Salt, $\left(C_6H_3\begin{cases}CO.OH\\SO_2.O-\\CH_3\end{cases}\right)_2Ba + 4H_2O$. — The method of preparation of this salt was the following: A solution of the free acid was taken, diluted to exactly 100 cc., divided into two portions of 50 cc. each, with one of which an excess of barium carbonate was boiled, and, after filtration, the other portion added and the solution evaporated to crystallisation. Most beautiful crystals in the form of long, perfectly colorless, clear needles, radiating from nuclei, were formed in the solution, but immediately on exposure to the air became opaque and crumbled to a white powder. The following results were obtained on analysing the salt:

I. 0.3310 gram of the salt gave 0.1210 gram $BaSO_4$.

II. 0.2713 gram of the salt gave 0.0989 gram $BaSO_4$.

III. 0.2713 gram of the salt lost 0.0310 gram in weight at 235°.

	Calculated for $\left(C_6H_3\begin{cases}CO.OH\\SO_2.O-\\CH_3\end{cases}\right)_2Ba + 4H_2O$.	Found. I.	II.	III.
Ba	21.44	21.50	21.43	...
H_2O	11.27	...	...	11.41

Acid Calcium Salt, $\left(C_6H_3\begin{cases}CO.OH\\SO_2.O-\\CH_3\end{cases}\right)_2Ca + 4H_2O$. — This salt was prepared in just the same way as the corresponding barium salt, except that powdered Iceland spar was used instead of barium carbonate. The salt is very soluble in water, and crystallises from solution in thin cubical plates. The following are the results of analysis:

I. 0.1990 gram of the salt gave 0.0496 gram $CaSO_4$.

II. 0.2037 gram of the salt gave 0.0504 gram $CaSO_4$.

III. 0.1596 gram of the salt lost 0.0221 gram in weight on heating at 175°.

	Calculated for $\left(C_6H_3\begin{cases}CO.OH\\SO_3.O-\\CH_3\end{cases}\right)_2Ca+4H_2O$.	Found. I.	II.	III.
Ca	7.38	7.33	7.28	...
H_2O	13.28	...	...	13.33

If heated above 175° the salt continues to lose weight, but shows at the same time evidence of more deep-seated decomposition.

Acid Magnesium Salt, $\left(C_6H_3\begin{cases}CO.OH\\SO_3.O-\\CH_3\end{cases}\right)_2Mg+xH_2O$.—The method of preparation in the case of this salt was the same as that of the other acid salts, magnesium carbonate, however, being employed as reagent. It is almost as soluble in water as the corresponding neutral salt, yielding only a semi-crystalline crust on the bottom of the containing vessel after standing for more than a month over sulphuric acid in a desiccator. No analysis of the salt was made.

Action of Caustic Potash on the Neutral Potassium Salt.

In order to obtain still further evidence that the acid under investigation is that sulpho-para-toluic acid represented by the formula $C_6H_3\begin{cases}CO.OH\ (1)\\SO_3.OH\ (2)\\CH_3\ \ (4)\end{cases}$, the neutral potassium salt, $C_6H_3\begin{cases}CO.OK\\SO_3.OK\\CH_3\end{cases}$, was fused with caustic potash with the object of forming, by the replacement of the sulphoxyl group by the hydroxyl group, an oxy-para-toluic acid. According to expectation, the acid formed should be that represented by the formula $C_6H_3\begin{cases}CO.OH\ (1)\\OH\ \ (2)\\CH_3\ \ (4)\end{cases}$. This acid and its derivatives have been studied by Engelhardt and Latschinow,[1] Biedermann and Pike,[2] Oppenheim and Pfaff,[3] Ihle,[4] Iles and Remsen,[5] Jacobsen,[6] and Schall.[7] Its melting-point (uncorrected) is stated by Iles and Remsen to be 169°–170°; Jacobsen gives the temperature

[1] Ztschr. Chem. 1869, 623. [2] Ber. d. chem. Ges. **6**, 324. [3] Ibid. **8**, 889.
[4] J. prakt. Chem. [2] **14**, 461. [5] Ber. d. chem. Ges. **11**, 462.
[6] Ibid. **11**, 570. [7] Ibid. **12**, 820.

177° as the corrected melting-point. The acid is volatile with water-vapor. Its solution gives with ferric chloride a deep violet coloration.

Accordingly the dry neutral potassium salt was added to fused caustic potash, and the mass stirred until the salt had dissolved. After cooling, the contents of the crucible were dissolved in water and the solution acidified with hydrochloric acid, when a voluminous precipitate of white crystals was formed. These were filtered off, washed with cold water, dissolved in hot water, the solution boiled with a little bone-black, filtered, and the acid again crystalised, filtered out and dried. The melting-point as determined with the aid of a very accurate thermometer was 174.5°. The correction to be added to obtain the true melting-point was calculated and found to be between three and four degrees. This would give as the corrected melting-point 177.5°–178.5°. The acid is soluble in hot water with readiness; almost insoluble in cold water. It is volatile with water-vapor. The solution of the acid gives an intense violet color with ferric chloride solution. The appearance and behavior of the acid closely resemble those of its homologue, salicylic acid. The isomeric meta-oxy-para-toluic acid melts at 206°–207°. No salts of the acid were prepared.

Para-toluic Sulphinide.

The preparation of "methyl-saccharin," or para-toluic sulphinide, from para-toluidine has been already described. The substance as received from the manufacturers is a yellowish crystalline powder, only slightly soluble in cold water, quite easily soluble in hot; easily soluble in alcohol, less readily in ether. All the solutions of the substance, before treatment with bone-black, have a straw-yellow color. Determinations of the solubility in water of the *pure* sulphinide were made thus:

Two portions of 100 cc. each of a saturated aqueous solution (temperature = 15.5°) were evaporated to dryness. The residues weighed 0.1526 gram and 0.1491 gram respectively, the mean of which is 0.1508. This gives as the solubility of para-toluic sulphinide in cold water about 15 parts in 10,000.

Pure para-toluic sulphinide was prepared by boiling the hot aqueous solution with bone-black and filtering, when, as the solution cooled, the sulphinide separated in very fine white needles. If the solution be not saturated and if the cooling take place

slowly, these crystals attain a length of one or two inches, are about a twentieth of an inch in width, and are very thin and flat. They are probably monoclinic. Thus crystallised, the sulphinide has the composition expressed by the formula $C_6H_3\begin{cases}CO\\SO_2\\CH_3\end{cases}>NH + \frac{1}{2}H_2O$, as is indicated by the results obtained on analysis:

I. 0.2989 gram of the sulphinide gave 0.5079 gram CO_2 and 0.0928 gram H_2O.

II. 0.2292 gram of the sulphinide gave 0.3925 gram CO_2 and 0.0803 gram H_2O.

III. 0.2307 gram of the sulphinide gave 0.01576 gram N.[1]

	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\CH_3\end{cases}>NH$.	Calculated for $C_6H_3\begin{cases}CO\\SO_2\\CH_3\end{cases}>NH + \frac{1}{2}H_2O$.	Found. I.	Found. II.	Found. III.
C	48.73	46.60	46.33	46.71	...
H	3.55	3.91	3.45	3.89	...
N	7.11	6.80	...	...	6.83

As was the case with ortho-sulpho-para-toluic acid, the combustions were made by burning the substance with lead chromate and lead oxide according to the method devised by Mr. R. De Roode.[2] The nitrogen was determined by the Kjeldahl method. The same difficulty was met with in the case of the sulphinide as in that of the free acid when the attempt was made to determine the "water of crystallisation" by heating the substance and noting the loss in weight. Heated at 190° the sulphinide gradually loses weight, but as soon as the substance has been rendered anhydrous, that is, when the weight has been reduced by an amount closely approximating a half-molecule of water, the residue begins in part to volatilise and in part to decompose, as is rendered evident by the fumes given off and by the change in color of the residue.

Pure para-toluic sulphinide melts at 249°–250°. It possesses an intensely sweet taste, which is followed by a decidedly bitter taste after the sweet has disappeared. I have made no comparison of the intensity of the sweet taste of para-toluic sulphinide with that of benzoic sulphinide.

When heated in dry condition in a test-tube, para-toluic sulphinide sublimes to some extent, but the greater part decomposes with carbonisation.

[1] Mr. J. H. Holmes kindly made this determination for me. [2] This Journal **12**, 226.

Salts of Para-toluic Sulphinide.

Like benzoic sulphinide, para-toluic sulphinide is a monobasic acid, it being possible to replace the hydrogen atom of the imido group by the atom of a univalent metal. Three of these salts were prepared, *viz.* those of barium, calcium, and silver.

I. *Barium Salt*, $\left(C_6H_3\begin{cases}CO\\SO_2>N-\\CH_3\end{cases}\right)_2 Ba + 5H_2O$.—This salt was prepared by boiling a solution of para-toluic sulphinide with an excess of pure barium carbonate, filtering and evaporating. The salt crystallises very well, the form being triclinic. It is quite soluble in water. Analysis of this salt gave the following results:

I. 0.17355 gram of the crystallised salt gave 0.0649 gram $BaSO_4$.

II. 0.1938 gram of the crystallised salt lost 0.0281 gram in weight when heated for some time at 145°.

Calculated for $\left(C_6H_3\begin{cases}CO\\SO_2>N-\\CH_3\end{cases}\right)_2 Ba + 5H_2O$.		Found. I.	Found. II.
Ba	22.13	22.00	...
H_2O	14.54	...	14.48

II. *Calcium Salt*, $\left(C_6H_3\begin{cases}CO\\SO_2>N-\\CH_3\end{cases}\right)_2 Ca + xH_2O$.—When a solution of para-toluic sulphinide is treated with powdered Iceland spar, the calcium salt is obtained. It is exceedingly soluble in water, as is the corresponding salt of benzoic sulphinide. Its aqueous solution deposits crystals when concentrated by evaporation and placed in a desiccator with phosphorus pentoxide. The crystals are opaque white needles. No analysis of the salt was made.

III. *Silver Salt*, $C_6H_3\begin{cases}CO\\SO_2>N.Ag\\CH_3\end{cases} + 1\frac{1}{2}H_2O$.—This salt was obtained by adding a solution of silver nitrate to a solution of para-toluic sulphinide. The greater part of the salt was deposited as a white precipitate, but, on standing, clear, diamond-shaped, colorless crystals were formed in the solution. The crystals possessed very marked refractive power. The salt probably has the composition given above, only one analysis having been made on account of the small quantity of the pure material at hand. The result of this analysis is the following:

0.10205 gram of the silver salt gave 0.0485 gram Ag_2SO_4.

Calculated for $C_6H_3\begin{cases}CO\\SO_2\\CH_3\end{cases}>N.Ag + 1\frac{1}{2}H_2O$.		Found.
Ag	32.63	32.68

Anhydride of Ortho-sulpho-para-toluic Acid.

Dohme, in his work upon the derivatives of ortho-sulpho-benzoic acid, prepared the anhydride of the acid by heating the anhydrous acid with phosphorus pentoxide for a long time at 130°. In the hope of obtaining a similar derivative, some ortho-sulpho-para-toluic acid, which had been deprived of its water of crystallisation by heating for a long time at 135°–140°, was mixed with two or three times its weight of phosphorus pentoxide in a small flask through the stopper of which a piece of glass tubing was introduced, as recommended by Dohme, and the flask heated in a sulphuric-acid bath at 145°. The heating was continued twenty-four hours. At the end of that time the tube (which was of about one-half inch diameter) was lined with transparent white rhombohedra. The crystals were deliquescent; if exposed to the air, they rapidly became opaque and then dissolved in the moisture they had abstracted from the atmosphere. Heated with resorcin, a brilliant fluorescent substance was obtained. No analysis of the substance, which was probably the anhydride, $C_6H_3\begin{cases}CO\\SO_2\end{cases}>O$, of ortho-sulpho-para-toluic acid, was made.
$\quad\quad\quad

that the actual properties of the substance were masked. He gives 190° as the melting-point of the anhydrous acid: I find that the acid becomes anhydrous at 135°–140°, and when in that condition melts at 158°. A sulphonic acid insoluble in water and instable toward bases, would certainly be regarded as a curiosity. The fact that strong oxidising agents convert ortho-sulpho-para-toluic acid into sulphuric acid as one of the products, as in the determinations of sulphur made by Pearson's method, would seem to indicate the possibility of the oxidation of thio-thymol by nitric acid beyond the desired stage, and the consequent formation of sulphuric acid. This would not, of course, explain the insolubility in water, which he ascribes to the product.

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THE ACTION OF LIGHT ON SILVER CHLORIDE.

BY ROMYN HITCHCOCK.

In a communication to the American Association for the Advancement of Science, at the Toronto meeting, 1889, I gave the results of some experiments which showed that, contrary to the general opinion of chemists, the chlorine set free from silver chloride by light amounts to not less than six per cent. of the weight of the chloride.[1] The accuracy of these results has been fully borne out by subsequent work, but it is doubtful if even my latest experiments, which show a loss of chlorine of over 8.5 per cent., have been carried far enough to represent the final effect of the light upon this compound. Indeed I may say almost with certainty that a still longer exposure of the films to sunlight would have shown a further loss. But I was obliged to stop my work quite suddenly and to leave undone several investigations which I had hoped to complete before publishing anything more upon this subject. The results here given are not to be taken as final; they are but a record of progress in a course of investigation which is

[1] This Journal **11**, 474.

of great promise, and which I hope to take up once more after my return from the far East.

The method of investigation is the same as that hitherto adopted. A very dilute solution of silver nitrate is precipitated in a dark room with dilute chlorhydric acid, and the finely-divided chloride allowed to settle upon slips of thin glass such as are used for covering microscopic objects. After about ten days the clear supernatant liquid is drawn off with a siphon, and replaced with distilled water run in very slowly by means of a siphon with an almost capillary end. In this way thin, quite perfect films of silver chloride were obtained. These were exposed to sunlight for many days and occasionally weighed. It was found that there was a constant decrease in the weight of the slips, which continued up to the final weighings, after at least one hundred days of exposure to sunlight.

The details of the manipulations are unimportant. It need only be said that the glasses were cleaned with sulphuric acid and potassium dichromate, and placed in a desiccator over sulphuric acid. They were then weighed several times, coated with the silver chloride in the manner described, and after thorough washing, again placed in the desiccator and weighed. They were then exposed to light under glass. In order not to confuse the reader with unnecessary figures, only a sufficient number of weighings will be given to indicate the progress of the decomposition. Only five slips, numbered as below, were used in the investigation. All the weighings were made on a fine Bunge balance, for the use of which I am indebted to the courtesy of Dr. Carl Barus.

Table I, showing the weights of the glass slips and of the silver chloride before exposure to light:

	Thin Glass, Average.	Glass + AgCl, Average.	Wt. of AgCl, Feb. 7.
I.	.41058	.43680	.02622
II.	.41051	.43437	.02386
III.	.41452	.44273	.02821
VI.[1]	.56131	.60112	.03981
IX.[1]	.63388	.67537	.04149
			Total AgCl, 0.15959

Table II, showing successive weights of slips after exposure to light:

[1] Slips VI and IX were of greater area than the others.

	Feb. 11.	Feb. 13.	Feb. 20.	July 12.	Aug. 25.
I.	.43576	.43542	.43529	.43504	.43491
II.	.43318	.43285	.43270	.43256	.43241
III.	.44143	.44098	.44083	.44053	.44041
VI.	.59948	.59882	.59858	.59764	.59743
IX.	.67401	.67342	.67306	.67181	.67130(?)

Table III, showing the loss in weight from the weighings in Table II, calculated for 0.1 gram AgCl:

	Feb. 11.	Feb. 13.	Feb. 20.	July 11 and 12.	Aug. 25.
I.	.00396	.00526	.00575	.00671	.00720
II.	.00498	.00637	.00700	.00758	.00821
III.	.00468	.00620	.00673	.00779	.00822
VI.	.00414	.00575	.00638	.00874	.00929
IX.	.00327	.00470	.00556	.00858	.00989(?)

A few words will explain some of the discrepancies noticeable in this table. Up to February 20th the slips were exposed to the sun in a small box with a glass cover. At that time it was observed that slips I and IX, which were at the ends of the box, were losing weight less rapidly than the others. The reason was that these two slips were partly shaded from the sun, mornings and afternoons respectively, by reason of their positions. The box was thenceforth discarded and the slips placed under beaker-covers. The last weighing of slip IX shows a loss greater than that due to the action of light—perhaps owing to mechanical injury to the film. This will be obvious if the weighings of the column of July 12th are compared with those of August 25th, for the loss of slip IX between the two weighings there appears more than twice as great as it should be. Rejecting this slip therefore, and also slip I as being below the truth for the reason given above, we may give the average loss in these experiments as 8.57 per cent. of the silver chloride used. This result is certainly well within the truth. The full extent of the decomposing action of light has not yet been reached. The course of dissociation is continuous during a long period of time, and can only be followed by the use of very finely-divided chloride spread in extremely thin films. It would be a rather surprising discovery, considering the literature of this subject, if it should be found that light effects the complete dissociation of silver and chlorine. But already one-third of the total chlorine is shown to be set free, and the process was certainly not complete.

Having observed such an unexpectedly large loss of chlorine in the manner described, it becomes of interest to know the composition of the resulting compound. This is a subject for more careful investigation in future, but as to first results I may say that warm dilute nitric acid dissolves from the exposed chloride a quantity of silver which corresponds to the amount of chlorine set free.

The bottom of the jar in which the slips were coated was more or less covered with the finely-divided precipitate. This was exposed to sunlight, then scraped off into a watch-glass and again exposed to the light for many days, with occasional stirring with a platinum wire. It was then weighed, treated with nitric acid and the silver determined in the solution. The results were as follows: AgCl darkened by light, 0.10141; AgCl from nitric acid solution, 0.03031, corresponding to Cl, 0.0075.

Not knowing the exact weight of the fresh, unexposed chloride used in this experiment, we cannot calculate the percentage of chlorine set free by the light, but the amount is obviously about 7 per cent. The analysis shows that the exposed and well-darkened chloride contains 22.5 per cent. of silver soluble in nitric acid—rather less than one-third the total amount of silver present in the pure chloride. But there is every reason to believe that the discolored chloride was still subject to the further action of light.

After the final weighing on August 25th, the five slips, which had been exposed to light for about four months, were placed in a beaker and digested with dilute nitric acid. The dissolved silver was determined as chloride, but before I could complete the analysis I was obliged to leave Washington. I am indebted to Dr. W. Hallock for collecting and weighing the precipitated chloride. The weight of silver chloride found by Dr. Hallock was 0.05588 gram, which is equivalent to 0.01382 of chlorine and 0.04205 of silver. From the weighings of August 25th we find the total loss of chlorine on the five slips to be .01393, which is perhaps excessive by reason of including slip IX, as already explained. This error, however, cannot well exceed three-tenths of a milligram, and is probably less. Comparing the results, we have: Loss of chlorine observed by weighings, 0.01393; chlorine calculated from silver dissolved by nitric acid, 0.01382. From this it would seem that the action of light is

merely to separate the chlorine from the silver, leaving the latter soluble in nitric acid, and it is of interest to observe that the quantity of silver thus rendered soluble is exactly equivalent to the weight of chlorine set free by the light.

Finally as a summary of results we have:

Original weight of AgCl, ...	0.15959
Weight of Cl lost, ...	0.01393
Per cent. of loss, ...	8.57
Silver rendered soluble in HNO_3, . . .	0.04205

Composition of AgCl after action of light:

Weight of discolored AgCl, ...	0.14566
Silver soluble in HNO_3, ...	0.04205
Per cent. of soluble silver, ...	28.8

I am not much disposed to assign a formula to a compound of such very inconstant composition, but premising that I regard it only as a mixture of metallic silver and silver chloride, the proportions of these two constituents would be approximately represented by the formula $(AgCl)_2Ag$.

S. S. PARTHIA, NEARING THE COAST OF JAPAN, *Sept.* 24, 1890.

NOTES.

A New Optically Active Lactic Acid.

While examining the water of a well for the *Anthrax bacillus*, Dr. Schardinger recently found[1] a micro-organism which, brought into a medium containing carbohydrates, caused active fermentation; if the liquid contains cane-sugar, the chief products of fermentation are alcohol and a lactic acid which turns the plane of polarisation to the right. According to the theory of LeBel and Van't Hoff concerning the optical properties of organic compounds, inactive ethylidene-lactic acid should be decomposable into two optically active isomers, as it contains an asymmetric carbon atom. Pasteur and Lewkowitsch found that

[1] Monatsh. Chem. **11**, 545 (1890).

certain micro-organisms, brought in contact with inactive tartaric acid in a suitable culture-medium, destroy one half of the acid, and that the remaining half becomes laevo-rotatory. Lewkowitsch treated inactive phenyl-glycolic acid with the organism *Penicillium glaucum*, and this destroyed the laevo-rotatory half, leaving the dextro-rotatory intact. Lewkowitsch treated inactive ethylidene-lactic acid with this same organism, obtaining a dextro-rotatory variety identical with para-lactic acid. So, later, Maly, and Nencki and Silber found that other organisms feeding on inactive ethylidene-lactic acid left the dextro-rotatory, but till now a laevo-rotatory acid has not been known. The author's method of work was that of Fitz; he added to 1 liter water 30 grams sugar, 10 grams ammonium chloride, 0.2 gram magnesium sulphate, 1 gram disodium phosphate, and 15–20 grams calcium carbonate. This mixture, which has an alkaline reaction, was carefully sterilised by continued treatment in a current of steam. Then a pure culture of the organism was added, and the flasks containing the mixture kept from 12–14 days at 36°. In 24–36 hours fermentation was noticeable, and it reached its maximum on the fourth or fifth day, and ceased 7–8 days after. By evaporating the acid contents of the flasks to crystallisation, Schardinger obtained a calcium salt of the new acid. 60 grams sugar yielded on an average 50 grams of this salt. By removing the calcium with oxalic acid and boiling the filtrate from the calcium oxalate with zinc carbonate, a zinc salt was obtained, identical in its chemical behavior and composition with zinc para-lactate. The free acid obtained from the zinc salt is a yellow, heavy, acid liquid, soluble in water, alcohol and ether. The silver salt was also made and analysed. The acid is laevo-, the salts dextro-rotatory, while para-lactic acid is dextro- and its salts laevo-rotatory.

If the new acid be mixed with a little alcohol or ether and allowed to stand in a desiccator over concentrated sulphuric acid, it loses water and becomes dextro-rotatory. Wislicenus has shown that para-lactic acid under similar conditions forms laevo-rotatory ester-anhydrides.

On mixing equal parts of solutions of the new zinc lactate and of zinc para-lactate, and evaporating, inactive zinc ethylidene-lactate crystallises out. The author has thus proved that inactive zinc ethylidene-lactate is made up of two optically active zinc lactates, and there can be no doubt that ordinary lactic acid consists of equal parts of dextro- and laevo-rotatory lactic acids, the case being analogous to that of tartaric and phenyl-glycolic acids. E. RENOUF.

An Optically Active Glyceric Acid.

The Journal of the Chemical Society for February, 1891, brings, under the above title, an article by Percy F. Frankland and Wm. Frew, describing an acid formed by the action on calcium glyce-

rate of a micro-organism called by them *Bacillus ethaceticus*, on account of its power to decompose mannite and glycerin into alcohol and acetic acid. Glyceric acid, $CH_2OH—CHOH—COOH$, contains an asymmetric carbon atom, and should, according to the theory of LeBel and Van't Hoff, be capable of existing in three isomers: the optically inactive form, and its components, the dextro- and laevo-rotatory forms. Hitherto, only inactive glyceric acid has been isolated, though Lewkowitsch, in his experiments with *Penicillium glaucum*, referred to in the preceding abstract, found that by growing this organism in a solution of ammonium glycerate the liquid became laevo-rotatory, but he did not follow up the investigation. Frankland and Frew find that when the *Bacillus ethaceticus* acts on a weighed quantity of the optically inactive calcium glycerate, under suitable conditions, it destroys one half of the salt, and the remaining half is laevo-rotatory. The pure acid obtained from the calcium salt was found to be dextro-rotatory. On heating aqueous solutions of the acid on the water-bath for some time, a white substance nearly insoluble in water is formed, which is powerfully laevo-rotatory. The authors believe this to be the anhydride of the acid, and consider the case analogous to that of the dextro-rotatory para-lactic acid and its laevo-rotatory ester-anhydrides as studied by Wislicenus. It now only remains to isolate in some way the laevo-rotatory glyceric acid, and from mixtures of the two optically active acids to build up the inactive variety, to complete the series of the glyceric acids demanded by the theory, as has been done with the series of tartaric, phenyl-glycolic and lactic acids.

E. Renouf.

The Constitution of Benzene and Related Hydrocarbons.

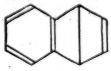
Julius Thomsen[1] has again applied thermic methods to the determination of the constitution of benzene and other ring compounds. Applying to trimethylene the formula $f\,C_aH_{2b} = ax + 2by - \Sigma v + 0.58$ C., in which x represents the heat of combustion of gaseous atomic carbon, y that of hydrogen attached to carbon, and Σv the caloric value of the linkages or bonds, the calculated heat of combustion is found to agree with that found, only on the assumption that trimethylene contains three half-double bonds, or, in other words, that the union of the two carbon atoms in trimethylene is just one half as strong as the union of the two carbon atoms in ethylene. From this we may conclude that a "double bond" is really composed of two single bonds, which neutralise each other to a certain extent. Thomsen suggests this, and will probably test the hypothesis later.

Applying the above formula to benzene, naphthalene, anthracene, phenanthrene and chrysene, it is found that the bonds have

[1] Zeits. für phys. Chem. **7**, 55.

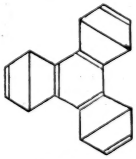
different thermic values from those of gaseous aliphatic derivatives, and that the difference is not entirely due to the solid state of the aromatic compounds. Stohmann's figures are used, and as these are practically identical for anthracene and phenanthrene, these two compounds are considered as having equal numbers of single and double bonds, and are therefore treated as one. Benzene, naphthalene and chrysene are considered as belonging to one series, the others to another, as the difference between the heat of combustion of benzene and that of naphthalene is just one half the difference between the latter and that of chrysene, and the value obtained for anthracene varies perceptibly from the mean of the values of naphthalene and chrysene. It is easily seen that if this is correct there must be more than one kind of linkage in these substances, and this conclusion is confirmed by the fact that the assumption of single bonds only leads to a greater heat of combustion for solid than for gaseous methane. Stohmann's figures are: Benzene, 777.3 C.; naphthalene, 1232.4 C.; anthracene, 1694.3 C.; phenanthrene, 1693.3 C.; chrysene, 2140.3 C.; and only by ascribing to benzene three, to naphthalene four, and to each of the others six double bonds, can Thomsen's formula be used. This gives the following graphic formulae:

Benzene.



Naphthalene.

Anthracene.



Chrysene.

If the thermic value of a single linkage be expressed by v_1, and that of a double by v_2, we find that in gaseous aliphatic derivatives $v_1=\frac{x}{2}-53.08$ C., and $v_2=x-121.63$ C., in solid paraffin $v_1=\frac{x}{2}-50.7$ C., and in solid aromatic compounds $v_1=\frac{x}{2}-49.09$ C., and $v_2=x-105.47$ C. The value of v_1 varies but slightly, that of v_2 greatly, and though the heat of combustion of a paraffin is increased 15.47 C. by the introduction of a double bond, that of an aromatic hydrocarbon is augmented but 7.29 C. If we adopt Thomsen's value for x, viz. 135.34 C., the values of v_1 and v_2 are

in olefines 14.59 C. and 13.79 C. respectively, v_1 being the greater, and in aromatic compounds 18.58 C. and 29.87 C., the double bond being much the stronger and hence very different from the olefine double bond. 29.87 C. may also be considered as the sum of the values of two single bonds of unequal intensity, and benzene would then contain nine bonds, six of normal and three of abnormal value, the six stronger being the peripheral, the three weaker the centric linkages.

Thomsen seems not to have noticed the rather remarkable result which follows the acceptance of his value for x, $x = 135.34$, and his formula for the thermic value of the triple bond, $v_3 = \frac{3}{2}x - 203.18$. If we substitute for $\frac{3}{2}x$ its value 203.1, we get $v_3 = 203.01 - 203.18 = -.17$; and if v_3 is less than zero, it is difficult to conceive how the acetylene condition can exist. Hence there seems little doubt that $x > 135.34$, and that the heat-value of the reaction $C,O = CO$ is greater than that of $CO,O = CO_2$.

F. LENGFELD.

Prof. Mendelejeff on Hydrazoic Acid.

Interest in the remarkable discovery of Curtius[1] has been considerably heightened through the publication by Prof. Mendelejeff[2] of an essay which deals with the subject of hydrazoic acid and its relations to other compounds, in a broad way thoroughly characteristic of its author. In the following review the attempt will be made to bring forward the points of special interest in this paper.

If any element R form with a univalent element X[3] a compound RX_n, then R will form an hydroxide $RO_{\frac{m}{2}}(OH)_{n-m}$, in which, however, the number of oxygen atoms must not be greater than *four*. For it is a feature of the Periodic System that (1) the sum of the numbers representing respectively the highest valencies of the element toward hydrogen and toward oxygen shall be equal to *eight;* and that (2) the number of hydroxyl groups which a given element can retain in combination and still form a compound capable of isolation, is the same as the number of hydrogen atoms contained in the hydrogen compound of that element—if such a compound exist. Thus suppose an element R form a hydride RH; then the oxides of that element will have as limits the compounds R_2O and R_2O_7. If the hydride be RH_2, the oxides will be limited by that having the formula RO_2; if RH_3 or RH_4, then the oxides exhibiting the highest valency will be R_2O_5 or RO_2, as the case may be. Besides, the hydroxides showing the highest valency, which exist in a free state, will be $RO_2(OH)$, $RO_2(OH)_2$, $RO(OH)_3$ and $R(OH)_4$, respectively. It will be seen that the number of oxygen atoms in these hydroxides is never greater than *four*.

It therefore follows (1) that an element R, which—as is the case

[1] Ber. d. chem. Ges. **23**, 3023. [2] Ibid. **23**, 3464.
[3] Of course it will be evident that X cannot be *hydrogen*.

with nitrogen—forms a hydride RH_3 and a highest oxide R_2O_5, cannot yield a hydroxide $R(OH)_5$ which will exist in the free condition and form salts: it may, however, form a hydroxide $R(OH)_3$. On the other hand (2) the highest hydroxide which can yield salts is derived from that which we call the normal hydroxide, through loss of the elements of water: thus—

$$PH_3O_4[=PO(OH)_3]=P(OH)_5-H_2O;$$
$$P_2H_4O_7[=\}PO(OH)_3\{_2O]=2P(OH)_5-3H_2O; \text{ and}$$
$$PHO_3[=PO_2(OH)]=P(OH)_5-2H_2O.$$

Finally (3) the ammonium salts characteristic of an element, being derived from these hydroxides, must contain other oxygen atoms in addition to those by means of which the ammonium radicle is held in combination. We thus have the salts, $NO_2(ONH_4)$, $SO_2(OH)(ONH_4)$, $SO_2(ONH_4)_2$, $CO(OH)(ONH_4)$, $CO(ONH_4)_2$, $CHO(ONH_4)$, etc.

These ammonium salts, by loss of the elements of water, yield (1) amides and (2) nitriles. Thus ammonium formate, $HCO(ONH_4)$, yields (1) formamide, $HCO(NH_2)$, and (2) hydrocyanic acid, HCN. Now since nitrogen and phosphorus form the hydrides NH_3 and PH_3, respectively, the highest hydroxides which they can produce are—

Meta: $N_2O_5.H_2O[=2NO(OH)_3-2H_2O]=2HNO_3$; and
$P_2O_5.H_2O[=2PO(OH)_3-2H_2O]=2HPO_3$:

Pyro: $N_2O_5.2H_2O[=2NO(OH)_3-H_2O]=H_4N_2O_7$; and
$P_2O_5.2H_2O[=2PO(OH)_3-H_2O]=H_4P_2O_7$:

Ortho: $N_2O_5.3H_2O[=2NO(OH)_3]=2H_3NO_4$; and
$P_2O_5.3H_2O[=2PO(OH)_3]=2H_3PO_4$.

The normal acids, as, for example, $N_2O_5.5H_2O[=2N(OH)_5]$, belong to the class of unstable compounds which may be considered to exist in the form of solutions.

While on the one hand phosphorus forms with hydrogen a compound less stable than ammonia, so on the other hand its highest oxide is far more stable than nitric anhydride. Orthonitrates do not exist. Among the ammonium salts only the metanitrate is known; still we can conceive of salts of the composition $NO(OH)(ONH_4)_2$ and $NO(ONH_4)_3$, respectively—secondary and tertiary ammonium orthonitrates. These would yield amides, $NO(OH)(ONH_4)NH_2$ and $NO(ONH_4)_2NH_2$: substances of the same composition as these two amides have been actually prepared through the action of dry ammonia gas on ammonium nitrate in solution.

By further abstraction of the elements of water from the amides, we might expect to obtain nitriles. Thus the nitrile of ammonium nitrate would be nitrous oxide; of the secondary and tertiary ammonium orthonitrates, hydrazoic acid and its ammonium salt, respectively:—

$NH_4NO_3 - 2H_2O = N_2O$;
$NO(OH)(ONH_4)(NH_2) - 3H_2O = N_3H$; and
$NO(ONH_4)_2(NH_2) - 3H_2O = N_4H_4$.

If we study the formation, from the ammonium salts, of the amides and nitriles of organic acids, we notice that one half the hydrogen in the ammonium radicle passes off with the oxygen atom which served to connect the ammonium radicle with the residue of the compound; and, when a further quantity of oxygen and hydrogen is eliminated, the hydrogen of the amido group passes out in combination with the oxygen of the carbonyl group; thus—

$$R.CO.O.NH_2.H_2 = R.CO.NH_2 + H_2O \text{; and}$$

$$R.C.O.N.H_2 = R.CN + H_2O:$$

so, in the case of the formation of hydrazoic acid from secondary ammonium orthonitrate, the reaction may be thus represented:

$$N\begin{cases} O \\ O.NH_4 \\ O.NH_4 \\ OH \end{cases} \rightarrow N\begin{cases} O \\ NH_2 \\ NH_2 \\ OH \end{cases} \rightarrow N\begin{cases} N \\ N. \\ H \end{cases}$$

The final product contains two nitrogen atoms originally combined with hydrogen in the form of ammonium radicles, and one which was originally contained in the nitric acid molecule: the hydrogen atom belonged to the acid residue, where it was present as hydroxyl, and consequently retains in hydrazoic acid its acid character. It is to be expected that, since nitrogen forms acids more energetic than those of carbon, the hydrogen of a nitrile of nitric acid will exhibit more marked acid properties than a corresponding derivative of an acid of carbon. On converting ammonium formate into formonitrile (hydrocyanic acid), the hydrogen atom, which in formic acid was not replaceable by metals, becomes acidic in the nitrile: there is reason therefore to look for very marked acid properties in hydrazoic acid. The greater acid-forming power of nitrogen, as compared with carbon, is seen when ammonia is contrasted with marsh-gas or ethane—the hydrogen of the ammonia is with much more ease directly replaceable by metals, as, for example, sodium. This we should be led to expect from a consideration of the relative position of the two elements in the Periodic System.

In this way Prof. Mendelejeff would explain the relative as well as the absolute acid-character of hydrazoic and hydrocyanic acids.

If now hydrazoic acid be a nitrile and, consequently, related to the cyanides, we should naturally look for some of the characteristic reactions of these compounds. Polymeric modifications of the acid or of its derivatives would be in order; the power to form double-salts corresponding to the ferrocyanides, etc., should

be noticeable; and the ability to pass over into isomeric modifications—as ammonium cyanate goes over into urea—is conceivable. The power to polymerise is much more noticeable in the case of compounds of phosphorus than with compounds of nitrogen—the former element exists in several isomorphous modifications: in the gaseous state its molecule consists of *four* atoms; still it is probable that some trace of this peculiarity may be found in derivatives of hydrazoic acid. Phosphame, which is its phosphorus analogue, is believed to be represented by the formula $(PN_3H)_n$.

If double salts of iron and potassium can be made, then we ought to be able to obtain two series of compounds corresponding to the ferro- and ferricyanides, which would give characteristic colored salts, of which those analogous to the ferricyanides would, in all probability, be violently explosive, if indeed they could exist at all in the free state.

The unsymmetrical ammonium cyanate, $CNO.NH_4$, can be transformed into the symmetrical urea, $CO.(NH_2)_2$; so, according to Mendelejeff, it may be possible to transform the unsymmetrical ammonium hydrazoate, $N_3.NH_4$, into the symmetrical diamide, $N.NH_2.NH_2.N$.

The author concludes with the hope that further investigation in this field will throw some light on what is really one of the darkest spots of the whole domain of chemical science—the chemistry of nitrogen.

WYATT W. RANDALL.

Hydrazoic Acid.

Curtius and Radenhausen publish in No. 4 of the Journal für praktische Chemie for 1891 a brief article describing the properties of hydrazoic acid, which they have succeeded in obtaining pure. They say that the very explosive nature of the acid makes it impossible to study its physical properties carefully, and it is largely with the object of warning chemists against making the dangerous anhydrous acid that they publish this notice, which suffices to prove that the acid can exist in an anhydrous condition, and to characterise it. Hydrazoic acid or azo-imide, N_3H, is a colorless liquid, boiling without decomposition at 37°; it mixes with water or alcohol, and has the terrible odor of the dilute acid intensified. It explodes in contact with heated substances, and sometimes without apparent cause at ordinary temperature, with unexampled violence, with evolution of brilliant blue light. Prof. Ostwald has studied the electrical conductivity of the acid, and thus finds it to be a somewhat stronger acid than glacial acetic acid. It is obtained by repeated fractional distillation of the aqueous acid. By this means a 91 per cent. acid was obtained, from which the remaining water was removed by calcium chloride. Hydrates, such as $N_3H + H_2O$ or $N_3H + 2H_2O$, do not seem to exist.

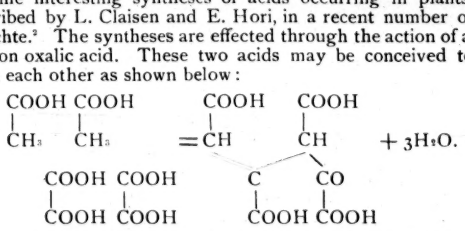
On bringing 0.05 gram of the acid into the barometric vacuum at ordinary temperature, it exploded, reducing the apparatus to dust and scattering the mercury in extremely small particles to the most distant corners of the very large room. 0.7 gram of the acid exploded apparently without cause on lifting the tube in which it was contained from the freezing mixture. Mr. Radenhausen was seriously injured, and all the glassware standing near the place of explosion was shattered.

Curtius promises to make a careful study of the acid and its derivatives, as solutions of the acid and salts are not so explosive. Mendelejeff's prophecy[1] that nitrogen ammonium (ammonium hydrazoate), N_4H_4, would undergo molecular rearrangement is not confirmed by experiment. Curtius finds that ammonium hydrazoate is a substance crystallising in large, shining prisms; its properties are not changed by sublimation nor by boiling its aqueous solution; the crystals are not hygroscopic, but volatilise slowly at ordinary temperature, first losing their brilliancy and disappearing completely in a few days; but the last residues of the salt treated with mineral acids yield unchanged hydrazoic acid.

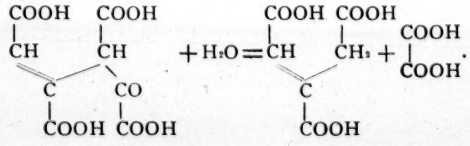
E. RENOUF.

Synthesis of some Organic Acids.

Some interesting syntheses of acids occurring in plants are described by L. Claisen and E. Hori, in a recent number of the Berichte.[2] The syntheses are effected through the action of acetic acid on oxalic acid. These two acids may be conceived to act upon each other as shown below:



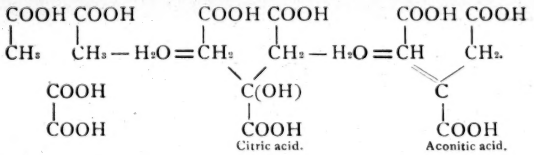
According to this, two molecules of acetic acid combine with two molecules of oxalic acid to form a tetrabasic acid which may be called *anhydro-diaceto-dioxalic acid* or *aconito-oxalic acid*, because it breaks down into oxalic and aconitic acids when treated with an alkali:



[1] Ber. d. chem. Ge. **23**, 3472.

[2] Ibid. **24**, 120.

The synthesis of aconitic acid takes place easily at the ordinary, or at slightly elevated, temperature, so that we might almost believe that in nature the formation of aconitic as well as that of citric acid takes place in the same way. Salts of acetic and oxalic acids are present in most plants. Both acids might unite directly as follows:



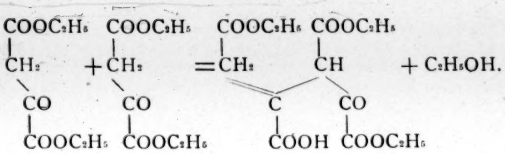
or they might first, and this appears to be the more probable view, unite to form *oxalacetic acid*, $COOH.CH_2.CO.COOH$, from which the other plant acids could be formed. Under the influence of the reducing processes in the plants this oxalacetic acid would be partly converted into malic acid, $COOH.CH_2.CH(OH).COOH$, and, from this, asparagine, $CONH_2.CH_2.CH(NH_2).COOH$, could easily be formed; while, according to the investigations of Von Pechmann, asparagine itself probably serves as the starting-point in the formation of a number of the vegetable alkaloids. By the action of ammonia upon aconitic and citric acids also pyridine derivatives are easily formed, as has been shown by Von Hofmann and Ruhemann; and the vegetable alkaloids probably owe their origin to some extent to these reactions.

As regards the means by which these condensations may be brought about in the plants, the authors point out that potassium acetate, which is always present, is itself a powerful condensing agent, and that it has been used by Lieben in this capacity in numerous condensations.

The experiment, which suggests the above remarks, consists in treating a mixture of ethyl acetate and ethyl oxalate with sodium ethylate. An ethereal salt of the formula—

$$\begin{array}{l} CH_2.COOC_2H_5 \\ | \\ CO \\ | \\ COOC_2H_5 \end{array}$$

, is thus formed, and this then undergoes further condensation, the product being the ethyl ether of aconito-oxalic acid:



By treatment with an alkali the ether yields aconitic acid.

I. R.

Resolutions adopted at a Conference of Chemists held in Philadelphia, December 30th and 31st, 1890, assembled to consider the formation of a national organisation.

Resolution 1. It is desirable that an American Association of Chemists be formed to embrace all existing American Chemical Organisations.

Resolution 2. Resolved, that this Conference recommend to all existing American Chemical Organisations that they call a meeting of their bodies to be held in Washington in connection with the meeting of the American Association for the Advancement of Science for 1891, and that each of these organisations be requested to appoint a committee, or to continue their present committee for the further discussion of the subject submitted to the Conference now in session.

Resolution 3. Resolved, that this general Conference Committee, composed of the present sub-committees, or such others as may be appointed by the several organisations, be called together at as early a time as practicable before the joint meeting recommended in Resolution No. 2.

Resolution 4. Resolved, that meanwhile each sub-committee, through its chairman, by correspondence or otherwise, shall formulate such modifications of the Constitution of the American Chemical Society as it shall deem necessary to adapt it to the requirements of the Association proposed.

Resolution 5. Resolved, that the chairmen of these sub-committees shall then, so far as possible, harmonise the views embodied in these reports of their several organisations, and shall have printed for presentation at the joint meeting a report, or majority and minority reports, on a Constitution for the proposed Association of American Chemists.

Voted that the Chairman of this Conference, with Professor Clarke and Professor Hale, be a committee of three to select time and place for the meeting called for in Resolution No. 3.

Voted to request the American Chemical Society to print the minutes of this Conference with their report of the proceedings of the Philadelphia meeting, and to mail copies as widely as possible to chemists in North America.

The Secretary of this Conference is desired to communicate the above resolutions to scientific journals with a view to obtain a wide publication of the same.

Adjourned to meet at call of the Chair.

H. CARRINGTON BOLTON,
Secretary of the Conference.

[The editor gladly publishes the above resolutions, and at the same time takes advantage of the opportunity to make a few comments on the subject of the proposed National Chemical Society. For many years past the subject has been discussed by the chemists of this country, and nearly twenty years ago an earnest effort was made to form an American society, with its headquarters at New York. For reasons which were almost entirely beyond the control of the gentlemen who were active in maintaining this organisation, it failed to become a national society in anything except its name. It is now proposed to try the same experiment, with Washington instead of New York as the headquarters. This has naturally awakened opposition on the part of the New York society, and it is, to say the least, doubtful whether the latter can be made to see the wisdom of the change. The writer ventures the prediction that, even if the New York society should yield its claims and become a section of the National Association, with headquarters at Washington, we should still have only a certain number of local societies, and should still lack the influence of a national organisation. The truth is, the conditions are unfavorable to the existence and usefulness of a national society in this country. There is no one place where there is a sufficient number of chemists of high standing to justify its selection as the headquarters of the society, and without some commanding section there would be something lacking. We have no London, no Paris, no Berlin. A section at Boston, or New York, or Philadelphia, or anywhere else would necessarily be local in its influence, and could not in any way control the society.

On the other hand, the writer is of the opinion that it would be a gain to chemistry to have some kind of an organisation that would bring the chemists of the country together more frequently. Such a society as the writer has in mind would not have any headquarters; its meetings would not be held for the sake of "papers"; it would not publish a journal; but it would furnish a good excuse for chemists to get together once or twice a year, and learn to know one another better. Hearty co-operation on some such basis as this would be of benefit. The editor will be glad to receive communications on the subject, and will publish in this Journal such as are appropriate, whether favorable or unfavorable to the general plan proposed.]